**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# GRAFT COPOLYMERIZATION OF STYRENE ONTO NATURAL RUBBER VIA EMULSION POLYMERIZATION

**M.Sc. THESIS**

**Burçin AKKUŞ**

**Department of Polymer Science and Technology**

**Polymer Science and Technology Programme**

**Thesis Advisor: Prof. Dr. Gürkan HIZAL**
**Anabilim Dalı : Herhangi Mühendislik, Bilim**
**Programı : Herhangi Program**

**JANUARY 2015**

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# GRAFT COPOLYMERIZATION OF STYRENE ONTO NATURAL RUBBER VIA EMULSION POLYMERIZATION

**M.Sc. THESIS**

**Burçin AKKUŞ**
**(515111035)**

**Department of Polymer Science and Technology**

**Polymer Science and Technology Programme**

**Thesis Advisor: Prof. Dr. Gürkan HIZAL**
**Anabilim Dalı : Herhangi Mühendislik, Bilim**
**Programı : Herhangi Program**

**JANUARY 2015**

**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

# EMÜLSİYON POLİMERİZASYONU İLE DOĞAL KAUÇUK ÜZERİNE STİREN AŞILANMASI

**YÜKSEK LİSANS TEZİ**

**Burçin AKKUŞ**
**(515111035)**

**Polimer Bilim ve Teknolojisi Anabilim Dalı**

**Polimer Bilim ve Teknolojisi Programı**

**Tez Danışmanı: Prof. Dr. Gürkan HIZAL**
**Anabilim Dalı : Herhangi Mühendislik, Bilim**
**Programı : Herhangi Program**

**OCAK 2015**

**Burçin AKKUŞ**, a **M.Sc.** student of ITU **Graduate School of Science and Engineering and Technology** student ID **515111035**, successfully defended the **thesis** entitled **"GRAFT COPOLYMERIZATION OF STYRENE ONTO NATURAL RUBBER VIA EMULSION POLYMERIZATION''** which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

| | | |
|---|---|---|
| **Thesis Advisor :** | **Prof. Dr. Gürkan HIZAL**<br>İstanbul Technical University | ..... |
| **Jury Members :** | **Prof. Dr. Ümit TUNCA**<br>İstanbul Technical University | ..... |
| | **Prof. Dr. Nergis ARSU**<br>Yıldız Technical University | ..... |

**Date of Submission : 15 December 2014**
**Date of Defense : 21 January 2015**

***To my precious family,***

## FOREWORD

This master study has been carried out at Istanbul Technical University, Institute of Science and Technology and at R&D Laboratory of CHT Textile Chemicals.

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Gürkan HIZAL for offering invaluable help in all possible ways, continuous encouragement and helpful critisms throughout this research.

I would like to also extend my sincere gratitude Assist.Prof.Dr.Aydan DAĞ for her friendly and helpful attitudes during my laboratory works. In addition, I would like to thank my group member Assoc.Prof.Dr.Hakan DURMAZ, Ufuk Saim GÜNAY, Neşe ÇAKIR, Elif BAYSAK for their support during my laboratory study.

I would like to thank my manager Canan DOĞAN and my colleague Seher ŞENADA for their sincerity and helpful attitude during my research.

I would like to thank my friends Ece ERTEM and Serkan AKPINAR for their favour, support and helpful attitude throughout my study.

I would like to offer the most gratitude to my family Hülya AKKUŞ, Refik AKKUŞ, Orçun AKKUŞ and my beloved Fatih GÜLER for their patience, understanding and morale support during all stages involved in the preparation of this research.

December 2014

Burçin AKKUŞ
(Chemist)

**TABLE OF CONTENTS**

**Page**

**ABBREVIATIONS**

**$^{1}$H NMR** **:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
**APS** **:** Ammonium Persulfate
**ASTM** **:** American Society for Testing and Materials
**$CDCl_3$** **:** Deuterated Chloroform
**FRP** **:** Free Radical Polymerization
**FTIR** **:** Fourier Transform Infrared Spectrophotometer
**GC** **:** Gas Chromatography
**NR** **:** Natural Rubber
**PS** **:** Particle Size
**St** **:** Styrene
**St-*g*-NR** **:** Styrene grafted Natural Rubber
**UV** **:** Ultraviolet

**LIST OF TABLES**

**Page**

**LIST OF FIGURES**

**Page**

## LIST OF SYMBOLS

| | |
|---|---|
| **$^{o}$C** | **:** Celsius |
| $T_g$ | **:** Glass-transition temperature |
| $M_n$ | **:** The number average molecular weight |
| $M_w$ | **:** The weight average molecular weight |
| $M_w/M_n$ | **:** The molecular weight distribution |
| **µm** | **:** Micrometer |

**GRAFT COPOLYMERIZATION OF STYRENE ONTO NATURAL RUBBER VIA EMULSION POLYMERIZATION**

## SUMMARY


NR has unique and special properties, including high tensile strength, high elongation, and outstanding resilience. It has gained more importance in industry due to its environmental preservation and being renewable source. However, natural rubber is weak in oil resistance, weather resistance, and ozone resistance because of unsaturated carbon double bonds.

Some curing techniques and physical and chemical modifications have been developed to get better weathering stabilization of natural rubber.

The chemical modification of NR by grafting with vinyl monomers combines the properties of NR and the monomer grafted. The most widely used vinyl monomers are methyl methacrylate, styrene, acrylonitrile. Many research in literature about the graft copolymerization of natural rubber have confirmed that St is one of the most suitable monomers when polymerized to give a high level of grafting, and also provides better ozone, heat, and weathering resistance.

Graft copolymerization of St onto NR molecule has been performed by free radical polymerization in emulsion states using various initiator systems including thermal and redox initiators. This work deals with the graft copolymerization of St onto NR in emulsion state by free radical polymerization.

The aim of this study was the graft copolymerization of Styrene (St) onto unsaturated carbon double bonds of Natural Rubber (NR) to improve the environmental resistance (UV, heat). The graft copolymerization of St onto NR was performed using ammonium persulfate (APS) as initiator in the emulsion polymerization at a temperature of 85 $^{0}$C for 4 hours. The graft copolymerization was also carried out by varying the concentrations of initiator and reaction temperature. The grafting efficiency, graft ratio, particle size, and monomer conversion results were compared.

The obtained copolymer composition was determined by nuclear magnetic resonance spectroscopy (NMR) and fourier-transform infrared spectrophotometer (FT-IR). The percentage of residual monomer was analyzed by gas chromatography (GC). The Styrene grafted Natural Rubber (St-*g*-NR) was applied as antislip carpet back-coating. The UV resistance and heat resistance of St-*g*-NR was tested by using accelerated weathering tester according to ASTM G154 Standard Practice for Operating Fluorescent Ultraviolet Lamp Apparatus for Exposure of Nonmetallic Materials.

# EMÜLSİYON POLİMERİZASYONU İLE DOĞAL KAUÇUK ÜZERİNE STİREN AŞILANMASI

## ÖZET

Serbest radikal polimerizasyonu bir zincir polimerizasyonudur. Monomerlerin aktif merkeze eklenmesiyle, polimer molekülü büyür. Her bir eklenmeden sonra serbest radikal, zincirin sonuna transfer olur. Serbest radikal polimerizasyonu 3 aşamadan oluşur. İlk aşama olan başlatma, başlatıcının radikal oluşturması ve bu serbest radikallerin monomer molekülüne eklenmesini kapsar. İkinci aşama olan ilerleme, monomer molekülünün aktif merkeze eklenmesiyle polimer zincirinin büyüdüğü aşamadır. Son aşama olan sonlandırmada, polimer zincirinin büyümesi durur. Bu sonlanma işlemi ya aktif zincirlerin çift oluşturarak kombinasyonu ile ya da hidrojenin aktif zincirle tepkimesiyle gerçekleşir.

Emülsiyon polimerizasyonu, bir çeşit serbest radikal polimerizasyonudur. En genel çeşidi, su içinde yağ (Y/S) emülsiyonudur. Monomer damlacıkları, suyun içinde emülsiye edilir. Bu emülsiyon çeşidi, dört bileşenden oluşur: emülsifiyer, monomer,başlatıcı ve dispersiyon ortamı.

Emülsifiyer (sürfaktan), bunun en önemli parçasıdır. Sürfaktanlar, hidrofobik kuyruk ve hidrofilik kafa kısmından oluşur. Belli bir konsantrasyona kadar sıvının yüzey gerilimini düşürürler. Bu nokta, kritik misel konsantrasyonudur. Kritik misel konsantrasyon noktasından sonra misel oluşumu başlar. Miseller, kolloid içinde disperse olmuş sürfaktan kümeleridir ve polimerleşme bu kümelerin içinde gerçekleşir.

Sürfaktanlar, kafa kısmının karakterine göre *i)* anyonik, *ii)* katyonik, *iii)* nanyonik, *iv)* amfoterik olarak sınıflandırılır. Özellikle endüstride, en çok tercih edilen sürfaktan, nanyonik/anyonik kombinasyonudur. Sinerjik etki yaratarak partikül boyutu kontrolü ve arttırılmış kolloidal stabilite sağlar.

Diğer bileşen, suda çözünmeyen ve serbest radikal polimerizasyonuna uygun monomerdir. Örneğin; bütadien, stiren, akrilatlar veya akrilik asitler gibi monomer veya monomer karışımları kullanılabilir. Önemli olan nokta, iyi şekilde disperse olmuş monomer emülsiyonu hazırlayarak sisteme vermektir.

Emülsiyon polimerizasyonu reaksiyonlarında, suda çözünebilen termal ya da redoks başlatıcılar kullanılabilir.

Y/S emülsiyon polimerizasyonlarında, dispersiyon ortamı olarak su kullanılır. Su mükemmel ısı transferi sağladığı için hızlı polimerizasyon oranlarında reaksiyon sıcaklığını kontrol etmek zor olmaz. Reaksiyon vizkozitesi çok yükselmez. Uçucu organik bileşikler bulundurmaz.

Emülsiyon bileşenleri, reaksiyon başlamadan evvel hazırlanıp karıştırılabilir. Bu, kesikli işlem olarak adlandırılır. Diğer bir yöntem, yarı-kesikli işlemdir. Reaksiyon boyunca, bileşenlerin belli aralıklarla sisteme beslenmesiyle gerçekleşir. Bu yöntem, daha iyi bir reaksiyon kontrolünü mümkün kılar. Uygun şartlar oluştuğunda, polimerizasyon mekanizması Smith-Ewart teorisine göre devreye girer.

Aşı kopolimerizasyonu, özel bir dallanmış kopolimer çeşididir. Yan zincirlerin yapısı, ana zincirden farklıdır. Aşı kopolimerizasyonu, 3 farklı şekilde gerçekleşebilir. i) *Grafting from:* Önceden belirlenmiş başlatıcı noktaları olan bir başlatıcı ile ikinci monomerin polimerizasyonu başlatılır. ii) *Grafting through*: Bir makromonomer ile düşük molekül ağırlıklı bir komonomer kopolimerize edilir. iii) *Grafting onto:* Fonksiyonel gruba sahip veya yaşayan bir polimer, başka bir polimerin fonksiyonel grubuyla çiftleşir.

Doğal kauçuk, poliizopren yapısının doymamış karbon çifte bağları nedeniyle *grafting onto* kopolimerizasyonuna uygun bir polimerdir. 1493 yılında Christoph Kolomb tarafından bulunduğundan beri büyük öneme sahiptir. Mükemmel mekanik özelliklerine rağmen, doymamış karbon çifte bağları yüzünden çevresel faktörlere karşı dayanımı düşüktür. Bu nedenle, fiziksel ve kimyasal olarak modifiye edilerek dayanımı arttırılır. Ya da kürleştirme işlemine tabi tutularak doymamış bağların çapraz bağlanarak doyurulması sağlanır.

Bu çalışmanın amacı, doğal kauçuğun çevresel faktörlere (UV, sıcaklık) dayanımını arttırmak için doymamış çifte karbon bağlarına stiren aşılanmasıdır. Stiren tercih edilmesinin sebebi, yapılan literatür çalışmaları sonrası veriminin yüksek olduğunun görülmesi, UV dayanımının olması ve maliyetinin düşük olmasıdır.

Stirenin doğal kauçuk üzerine aşı kopolimerizasyonu, amonyum persülfat başlatıcı ile 85$^{o}$C sıcaklıkta, 4 saatte gerçekleştirildi. Farklı başlatıcı konsantrasyonları ve farklı sıcaklıklarda kopolimerizasyon çalışması yapıldı. Böylece, başlatıcı miktarının ve sıcaklığın aşılanma verimine etkisi araştırıldı.

4 boyunlu reaktörle, 300 rpm dönme hızında çalışıldı. Reaktöre su, doğal kauçuk ve tampon çözeltisi konulup 30 dakika azot gazı ile içerisindeki oksijenden arındırıldı. Ayrı bir yerde, APS çözeltisi ile stiren monomeri, su ve anyonik/nanyonik sürfaktan karışımından oluşan monomer emülsiyonu hazırlandı. Reaksiyon sıcaklığına ulaşıldığında APS ve monomer emülsiyonu aynı anda sisteme beslenmeye başladı. Reaksiyon sonunda elde edilen emülsiye halde üründen örnek alınıp Gaz Kromatografi cihazı ile monomer dönüşümü hesap edildi. Dinamik ışık saçılımı yöntemiyle partikül boyutu ölçümü yapıldı.

Aşılanma verimi, aşılanma oranı sonuçları için emülsiyon %10 konsantrasyonlu $CaCl_2$ ile koagule edilerek deiyonize suyla yıkanıp etüvde kurutuldu. Reaksiyona girmemiş doğal kauçuk, homo-polistiren ve aşılanmış doğal kauçuktan oluşan katı haldeki ürün, Soxhlet ekstraksiyonu ile saflaştırıldı. Reaksiyona girmemiş doğal kauçuğu ayırmak için 24 saat boyunca 80 $^{0}$C petrol eteri ile ekstraksiyon yapıldı. Kalıntı 1gün boyunca etüvde kurutulup ikinci ekstraksiyon yapıldı. Metil eter keton: aseton karışımıyla 24 saat ekstrakte edilerek homo-polistirenden arındırıldı. Ayrılan her bir parçanın tartımları alınıp uygun formülasyonlar kullanılarak aşılanma verimi, reaksiyona girmemiş doğal kauçuk yüzdesi ve homo-polistiren yüzdesi hesaplandı. Safsızlığından arındırılmış stiren aşılanmış doğal kauçuk kopolimeri, FTIR ve $^{1}$H NMR metotlarıyla analiz edilerek fonksiyonel grupları belirlendi.

80 g/m$^2$ miktarında stiren aşılanmış doğal kauçuk ile aşılanmamış doğal kauçuk, halı sırtı kaplandı. UV dayanımı ve sıcaklığa karşı dayanımının test edilmesi için, hızlandırılmış yaşlandırma cihazı ile test edildi. 60 $^{0}$C'de 4 saat boyunca ve 50 $^{0}$C'de 4 saat boyunca nemli ortamda 315 nm dalga boyundaki UV lambasına maruz bırakılarak ASTM G154-00a standardına uygun olarak test edildi.

## 1. INTRODUCTION

Natural rubber (NR) obtained from *Hevea brasiliensis* recently has gained more importance in industry because the increased awareness about environmental preservation and an increased emphasis on the use of renewable resources [1].

NR has unique and special properties, including high tensile strength, high elongation, and outstanding resilience. It has been used in wide range of applications such as tires, rubber springs, vibration mounts, coatings etc. However, NR is an unsaturated rubber that consists of mainly cis-1, 4- polyisoprene [2] which makes it weak in oil resistance, weather resistance, and ozone resistance [3].

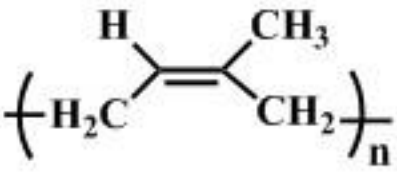


**Figure 1.1:** Structure of natural rubber

Normally, commercially available antioxidants can be added into the rubber formulations, such as benzophenone, benzotriazole, amines, phenolics, and phosphites antioxidants for the purpose of an enhancement durability of NR by protecting from UV degradation [4-8]. However, these organic antioxidants may cause incompatibility, migration, or decomposition during UV exposure [9-12].

Physical and chemical modifications have been developed to get better UV stabilization, and also to obtain improved properties for the production of new materials [13]. Among the chemical modifications of NR are epoxidation, hydrogenation, maleinization, and graft copolymerization [14].

The chemical modification of NR by grafting with vinyl monomers having better mechanical properties combines the properties of NR and the monomer grafted. The most widely used vinyl monomers are methyl methacrylate [15], styrene [13,16,17], acrylonitrile [18], dimethylaminoethyl methacrylate [19]. Research on NR has confirmed that St is one of the most suitable monomers when polymerized to

give a high level of grafting [1,20,21]. Moreover, the graft copolymer of St onto NR, comprising the rubbery core-glassy shell, provides better ozone, heat, and weathering resistance [21-24].

Graft copolymerization of St onto NR molecule has been performed by free radical polymerization (FRP) in solution or in emulsion states using various initiator systems including thermal initiators such as benzoyl peroxide, potassium persulfate, and redox initiators such as cumene hydroperoxide/tetraethylene pentamine, tert-butyl peroxide/tetraethylene pentamine, or potassium persulfate/sodium thiosulfate [25].

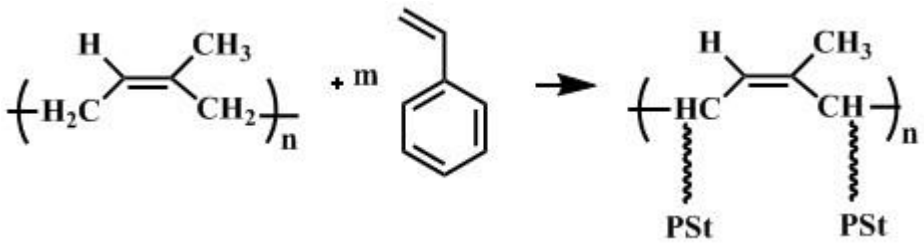


**Figure 1.2:** Schematic representation of graft copolymerization of St onto natural rubber

This work deals with the graft copolymerization of St onto NR in emulsion state by free radical polymerization. The graft copolymer of NR has been found to have much better weathering and heat resistance compared to NR. Furthermore, binding and antislip properties of graft copolymer in carpet back-coating applications have given successful results. Ammonium persulfate was used to create radicals on natural rubber backbone. The mixture of nonionic and anionic emulsifiers was chosen for the formation of reaction loci in aqueous media and for maintaining colloidal stability of latex. The drop wise monomer addition was continued during reaction time. Copolymers having core-shell morphology were synthesized due to this addition onto natural rubber. Then, the effects of temperature and initiator concentration on grafting were determined.

## 2. THEORETICAL PART

### 2.1 Emulsion Polymerization

Emulsion polymerization is frequently used in industry to produce latex paints, rubbers, coatings and adhesives. Approximately 15% of the Western world's $10^8$ tons/year of polymers is produced in emulsion polymerization processes [26].

Emulsion polymerization is a complex process in which the radical addition polymerization proceeds in a heterogeneous system. Relatively hydrophobic monomer emulsifies in water by an oil-in-water emulsifier, and then either a water-soluble or an oil-soluble free radical initiator triggers the initiation reaction. At the end of the polymerization, a milky fluid called "latex", "synthetic latex" or "polymer dispersion" is obtained. Latex is defined as "colloidal dispersion of polymer particles in an aqueous medium". The polymer may be organic or inorganic. In general, latexes contain 40-60 % polymer solids and comprise a large population of polymer particles dispersed in the continuous aqueous phase (about $10^{15}$ particles per mL of latex). The particles are within the size range 10 nm to 1000 nm in a diameter and are generally spherical. A typical particle is composed of 1-10000 macromolecules, and each macromolecule contains about $10^2$–$10^6$ monomer units [27-33].

The earliest literature references to produce synthetic latex are patents originated from Farbenfabriken Bayer in the years 1909 to 1912 [34,35]. These studies involved polymerization of diene monomers in the form of aqueous emulsions which are stabilized by gelatin, egg white (protein), starch, flour, and blood serum as protective colloids to produce something resembling natural rubber latex. Initiation of polymerization depended on aerial oxygen. But these attempts and other similar studies that followed them were substantially different from what is known today as "emulsion polymerization". In 1929, Dinsmore, who was working for The Goodyear Tire & Rubber Company, was the first to be granted a patent to produce a

synthetic rubber in the presence of soap as emulsifying agent [36]. Later, the practice of emulsion polymerization grew rapidly and industrial-scale production started in the mid-1930. The major developments in emulsion polymerization took place around the Second World War as a result of the intensive collaborative efforts between academia, industry and government laboratories. During and after World War II, the production of many types of latex both in homopolymers and copolymers of different composition was achieved by using different monomers such as butadiene, styrene, acrylic esters, acrylonitrile and vinyl acetate. A wide variety of initiating systems were used, and conversions of the polymerization reactions were increased.

Looking at the historical development of the emulsion polymerization, it is seen that the trigger factor in this development was the necessity for synthetic rubber in the wartime. The production of styrene/butadiene rubber (SBR) satisfied this requirement. Today, millions of tons of synthetic latexes are produced by the emulsion polymerization process for use in wide variety of applications. In the synthetic latexes, the most important groups are styrene/butadiene copolymers, vinyl acetate homopolymers and copolymers, and polyacrylates. Other synthetic latexes contain copolymers of ethylene, styrene, vinyl esters, vinyl chloride, vinylidene chloride, acrylonitrile, chloroprene and polyurethane.

In both of the large volume and the small volume applications, this variety of emulsion polymers and the widespread use of them are caused by emulsion polymerization which offers many kinetic and technological advantages over other polymerization methods. Emulsion polymerization has some clear advantages as compared to other types of free radical polymerization, being bulk, solution and suspension polymerization. The dispersion medium is water that provides inexpensive, nonflammable, nontoxic and relatively odorless systems. This polymerization has relative simplicity of the technological process. It is possible to produce high molecular weight polymer at a high reaction rates, and the viscosity of latex is independent of the molecular weight. Thus the producing of high solids content emulsions with low viscosity can be achieved in contrast to solutions of polymers. This method offers better temperature control during polymerization due to more rapid heat transfer in the low viscosity emulsion. There are possibilities of feeding the ingredients at any stage of reaction and the achievement of many

copolymerizations that consist of different monomers in wide variety physical properties. The control of undesirable side reactions such as chain transfers, and the range and distribution of particle size can also be obtained. In addition, the dry form of emulsion polymers can be used in many applications as well as the use of latex itself (in wet form) [37].

### 2.1.1 Main ingredients of emulsion polymerization

A typical emulsion polymerization formulation comprises four basic ingredients: 1) monomer, 2) dispersion medium, 3) emulsifier, 4) initiator. Further auxiliaries, such as chain transfer agents, buffers, acids, bases, anti-aging agents, biocids, etc., can be used.

#### 2.1.1.1 Monomer

Emulsion polymerization requires free-radical polymerizable monomers which form the structure of the polymer. The major monomers used in emulsion polymerization include butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, acrylic acid and methacrylic acid, and vinyl chloride. The first classification of emulsion polymerization process is done with respect to the nature of monomers studied up to that time. This classification is based on data for the different solubilities of monomers in water and for the different initial rates of polymerization caused by the monomer solubilities in water. According to this classification, monomers are divided into three groups. The first group includes monomers which have good solubility in water such as acrylonitrile (solubility in water 8%). The second group includes monomers having 1-3 % solubility in water (methyl methacrylate and other acrylates). The third group includes monomers practically insoluble in water (butadiene, isoprene, styrene, vinyl chloride, etc.) [29].

#### 2.1.1.2 Emulsifier

These materials perform many important functions in emulsion polymerizations [28,30,38] such as *(i)* reducing the interfacial tension between the monomer phase and the water phase so that the monomer is dispersed (or emulsified) in the water phase with agitation, *(ii)* generating micelles, *(iii)* stabilizing the monomer droplets in an emulsion form, *(iv)* serving to solubilize the monomer within emulsifier

micelles, *(v)* stabilizing the growing and final latex particles, *(vi)* acting to solubilize the polymer, *(vii)* serving as the site for the nucleation of particles, *(viii)* acting as chain transfer agents or retarders.

Emulsifiers (also referred to as surfactant, soap, and dispersing agent) are surface-active agents. These materials consist of a long-chain hydrophobic (oil-soluble) group (dodecyl, hexadecyl or alkyl-benzene) and a hydrophilic (water-soluble) head group. They are usually classified according to the nature of this head group. This group may be anionic, cationic, zwitterionic or non-ionic [38]. Anionic emulsifiers having negatively charged hydrophilic head group are the sodium, potassium and ammonium salts of higher fatty acids, and sulfonated derivatives of of aliphatic, arylaliphatic, or naphtenic compounds. Sodium lauryl (dodecyl) sulfate, [$C_{12}H_{25}OSO_3^-Na^+$], sodium dodecyl benzene sulfonate, [$C_{12}H_{25}C_6H_4SO_3^-Na^+$] and sodium dioctyl sulfosuccinate, [$(C_{18}H_7COOCH_2)_2SO_3^-Na^+$] are commonly used in emulsion polymerizations as anionic emulsifiers. Quaternary salts such as acetyl dimethyl benzyl ammonium chloride and hexadecyl trimethyl ammonium bromide may be given examples for cationic emulsifiers. Zwitterionic (amphoteric) emulsifiers can show cationic or anionic properties depending on pH of the medium. They are mainly alkylamino or alkylimino propionic acids. Non-ionic emulsifiers carry no charge unlike ionic emulsifiers. The most used type of these emulsifiers is that with a head group of ethylene oxide (EO) units. Polyoxyethylenated alkylphenols, polyoxyethylenated straight-chain alcohols and polyoxyethylenated polyoxypropylene glycols are the most commonly three classes of non-ionic emulsifiers used for emulsion polymerization formulations. Polyoxyethylenated alkylphenol type of emulsifiers includes two main members: nonylphenol polyoxyethylene glycol, [$C_9H_{17}C_6H_4O\text{-}(CH_2CH_2\text{-}O)_nH$], and octylphenol polyoxyethylene glycol, [$C_8H_{15}C_6H_4O\text{-}(CH_2CH_2\text{-}O)_nH$]. The number of EO units, (n), may be diversified from a few to about 100 (typically from 1 to 70 EO units), which characterize the distribution of polyEO chain lengths for each specific emulsifier.

In general, the anionic emulsifiers are extensively preferred in many emulsion polymerization systems. They serve as strong particle generators and stabilize the latex particles via electrostatic repulsion mechanism. But latexes stabilized with this type of emulsifiers are often unstable upon addition of electrolytes and in freeze-thaw cycles. Furthermore, these emulsifiers have limited stabilizing effectiveness at

high solids (>40%) and present high water sensitivity. To overcome these problems, non-ionic emulsifiers can be used to nucleate and stabilize the particles in the course of emulsion polymerization. In this case, it is the steric stabilization mechanism that protects the interactive particles from coagulation. In addition, the use of non-ionic types improves the stability of latex product against electrolytes, freeze-thaw cycles, water and high shear rates. As a result of them, in many emulsion polymerization recipes particularly in industry, mixtures of anionic and non-ionic emulsifiers have been widely used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability [39-41]. The cationic and zwitterionic emulsifiers are used infrequently in emulsion polymerization applications.

Besides all these types of emulsifiers, polymeric and reactive emulsifiers can be used in emulsion polymerizations. Polymeric emulsifiers are often non-ionic water-soluble polymers such as poly (vinyl alcohol), hydroxyethyl cellulose and poly (vinyl pyrrolidone), and called sometimes as a "protective colloid". They are used to increase the particle stability in latexes against coagulation. Reactive emulsifiers ("surfmers"), which have polymerizable reactive group, can copolymerize with the main monomer and be covalently anchored onto the surface of latex particles. When these compounds used in emulsion polymerizations, the emulsifier migration is reduced. Furthermore, surfmers improve the water resistance and surface adhesion as well as resistance against electrolytes and freeze-thaw cycles in comparison to conventional emulsifiers. Surfmers can be anionic with sulfate or sulfonate head groups (sodium dodecyl allyl sulfosuccinate), cationic (alkyl maleate trimethylamino ethyl bromide), or non-ionic (functionalized poly (ethylene oxide)-poly(butylenes oxide)copolymer). The reactive groups can be in different types, for example, allylics, acrylamides, (meth) acrylates, styrenics, or maleates [42,43].

#### 2.1.1.3 Initiator

Emulsion polymerization occurs almost entirely following the radical mechanism. The function of the initiator is to generate free radicals, which in turn lead to the propagation of the polymer molecules. The free radicals can be commonly produced by two main ways: *(i)* thermal decomposition, or *(ii)* redox reactions. In addition, the free-radical initiators can be either water or oil-soluble. The most commonly used water-soluble initiators are persulfates (peroxodisulfates). For example,

potassium-, sodium-, and ammonium-persulfate. Persulfate ion decomposes thermally in the aqueous phase to give two sulfate radical anions which can initiate the polymerization. Hydrogen peroxide and other peroxides are thermal decomposition type initiators and they are soluble in both the aqueous and monomer-swolen polymer phases. Besides of these, oil-soluble compounds such as benzoyl peroxide and azobisisobutyronitrile (AIBN) can be employed as thermal initiators in emulsion polymerizations. The other initiation system consists of redox initiators (such as persulfate-bisulfite system) which produce free radicals through an oxidation-reduction reaction at relatively low temperatures.

The main types of free radicals which are produced by thermally or redox system are:

a. Persulfates

$$S_2O_8^{-2} \rightarrow SO_4\bullet^{-1} + SO_4\bullet^{-1}$$

b. Hydrogen peroxide

$$HO-OH \rightarrow HO\bullet + HO\bullet$$

c. Organic peroxides

$$RO-OR^1 \rightarrow RO\bullet + R^1O\bullet$$

d. Azo compound

$$RN=NR^1 \rightarrow R\bullet + R^1\bullet + N_2$$

e. Persulfate-Bisulfite

$$S_2O_8^{-2} + HSO_3^{-1} \rightarrow SO_4\bullet^{-1} + SO_3\bullet^{-1} + HSO_4^{-1}$$

**Figure 2.1:** Free radical types of thermal and redox initiators

### 2.1.1.4 Other ingredients

The formulations of emulsion polymerization may include a wide variety of ingredients: *chain transfer agents* are added to a latex formulation to help regulate the molar mass and molar mass distribution of the latex polymer. The mercaptans are the most common type of chain transfer agents. The surface active transfer agents, *"transurfs"*, are also used in emulsion polymerizations. *Buffers* are often added to a latex formulation to regulate the pH of the polymerization system.

Generally, for this purpose, sodium bicarbonate has been chosen. In addition, coalescing aids, plasticizers, thickening agents, antimicrobial agents, antioxidants, UV-absorbers, pigments, fillers, and other additives can take place in a recipe of emulsion polymerization.

### 2.1.2 Mechanism of emulsion polymerization

In the emulsion polymerizations, the free-radical mechanism is very closely connected with the heterogeneous nature of the emulsion polymerization in which the micellar phase, the aqueous phase, the monomer droplet phase and the particle phase exist. After the emulsion of the monomer phase in the water phase and the presence of the emulsifier micelles established, the polymerization is initiated by the addition of initiator. According to the theories proposed by Harkins and Smith and Ewart [44,45], conventional emulsion polymerization mechanism occurs into three intervals including the initial stage, the particle growth stage and the completion stage.

#### 2.1.2.1 The initial stage (Interval I)

This stage is also called as "*particle formation*" or "*nucleation*". With the addition of initiator to the reaction mixture, the free-radicals which initiate the polymerization are generated in the aqueous phase and diffuse into monomer-swollen micelles. These micelles act as a meeting place for the hydrophobic monomer and the water-soluble initiator. Since they exhibit an extremely large oil-water interfacial area for diffusing of free-radicals and have high monomer concentration. On the other hand, a small amount of particle initiation can occur within the continuous aqueous phase. Monomer molecules dissolved in this phase are first polymerized by waterborne free radicals. This would result in the increased hydrophobicity of oligomeric radicals.

When a critical chain length is achieved, these oligomeric radicals become so hydrophobic that they show a strong tendency to enter the monomer-swollen micelles and then continue to propagate by reacting with those monomer molecules.

But this nucleation becomes less significant as the amount of micellar emulsifier in the system increases. The amount of polymerization occurring in the monomer

droplets is regarded as being a very minor proportion of the whole because of their small surface area for diffusing of the free-radicals.

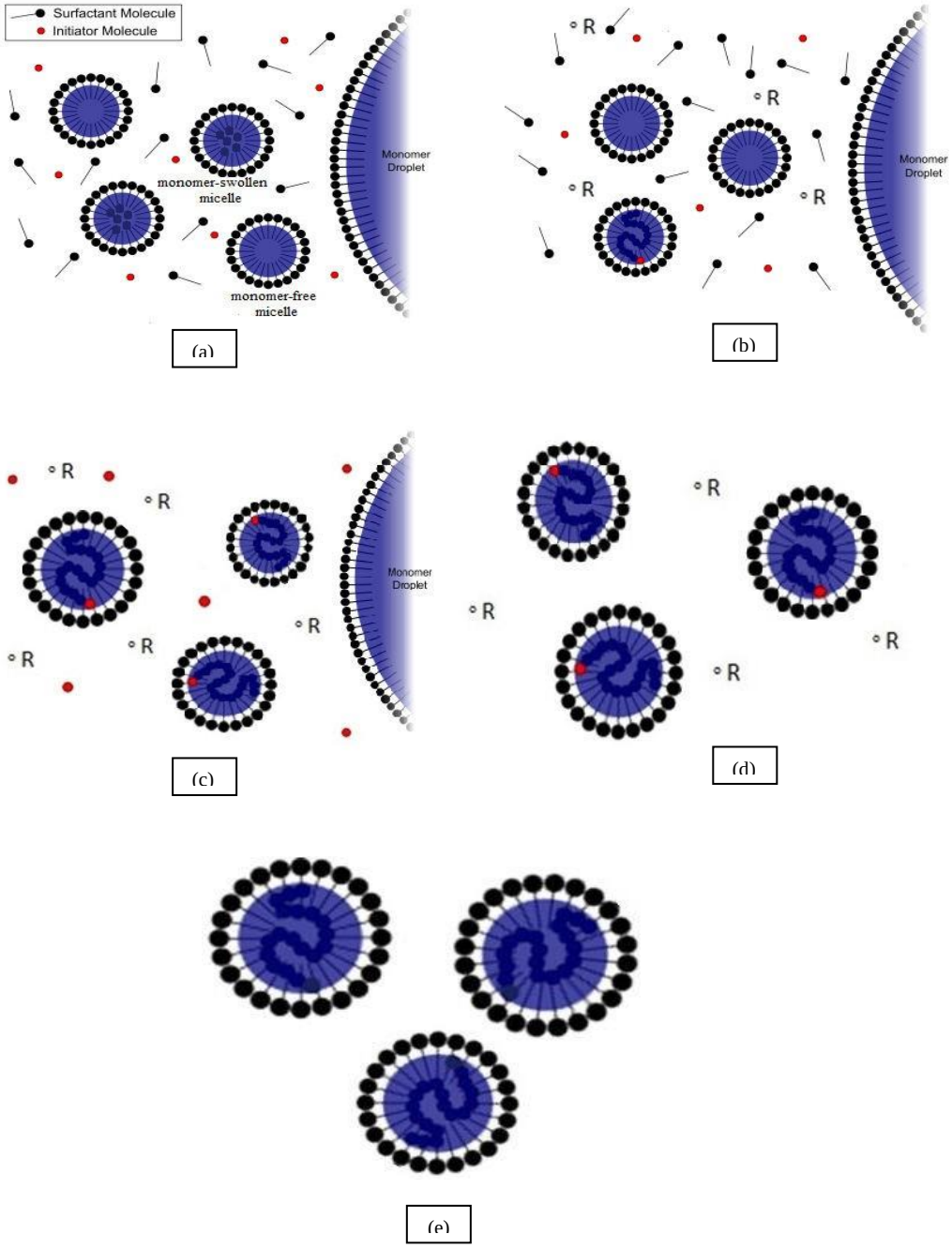


**Figure 2.2:** Schematic representation for the mechanism of emulsion polymerization [37]

As a result, monomer-swollen micelles are favored as the sites of the nucleation of polymer particles. Therefore, this nucleation mechanism, proposed by Harkins and Smith and Ewart and modified by Gardon, is called as "micellar" or "heterogeneous" nucleation [46].

After nucleation, monomer-swollen micelles are transformed into polymer particles swollen with monomer. With the continued adsorption of micellar emulsifiers onto growing particles, the micelles start to disappear (Figure 2.2.b). The particle nucleation stage (Interval I) ends with this disappearance of the micelles at relatively early in the reaction (e.g. between 10% and 20% conversion). During Interval I, the rate of polymerization increases with the increasing time of reaction and only one out of every 100-1000 micelles becomes a polymer particle. The number of particles nucleated per unit volume of water is proportional to the emulsifier concentration and initiator concentration to the 0.6 and 0.4 powers, respectively according to the Smith-Ewart theory. After the particle nucleation process is completed, this number remains relatively constant toward the end of polymerization.

#### 2.1.2.2 The particle growth stage (Interval II)

After the particle nucleation process is completed, polymerization proceeds homogeneously in the polymer particles as the monomer concentration in the particles is maintained at a constant concentration by diffusion of monomer from the monomer droplets. The rate of polymerization in this stage is constant. In addition, during this stage, the number of monomer-swollen polymer particles and the monomer/polymer ratio remain constant. The monomer droplets decrease in size as the size of the polymeric particles increase. When monomer droplets completely disappear in the polymerization system (at 50-80% conversion), the particle growth stage (Interval II) ends (Figure 2.2.c). In this situation, the polymer particles contain all the unreacted monomer and essentially all of the emulsifier molecules are also attached to the surface of polymer particles.

#### 2.1.2.3 The completion stage (Interval III)

This is the final stage of the reaction. In this stage, polymerization continues within the monomer-swollen polymer particles which were formed during Interval I, and persisted and grew during Interval II (Figure 2.2.d). In the ideal case, the number of reaction loci during this stage is essentially fixed at the number which had become formed at the end of Interval I. Whereas, the concentration of monomer in the reaction loci and the polymerization rate continues to decrease toward the end of polymerization. Finally, the polymerization is complete and the conversion of essentially 100% is usually achieved. The system now comprises a dispersion of

small polymer particles stabilized with the molecules of the original emulsifiers (Figure 2.2.e).

### 2.1.3 Types of emulsion polymerization process

Three types of process are commonly used in carrying out the emulsion polymerization: *batch*, *semi-continuous*, and *continuous*. This classification is made according to the way in which the Interval II and Interval III reactions are effected [47].

#### 2.1.3.1 Batch process

The batch-type process is the simplest method for effecting emulsion polymerization. All ingredients are placed in a reactor at the beginning of the reaction. The system is agitated, and heated to reaction temperature. Polymerization begins as soon as the initiator is added. Then, the reaction system is kept there by heating or cooling, as needed, and by agitating until the samples removed indicate the desired conversion of monomer to polymer. The only significant changes which can be made in such cases are to the reaction temperature, reactor design and the type and speed of agitation.

It is commonly used in the laboratory to study reaction mechanism and kinetics, but most commercial latexes are not manufactured by this process because of their undesirable properties. This process has the important disadvantages that limited control is exerted over either monomer/polymer ratio in the reaction loci, or over heat transfer in the reaction, or over copolymer composition. Nevertheless, batch process has an important role, particularly in more fundamental studies.

#### 2.1.3.2 Semi-continuous process

This process is very versatile and is widely used, both industrially and in academic laboratories. Semi-continuous (or semi-batch) emulsion polymerization offers great degree of operational flexibility than batch or continuous processes. It allows one great control over the course of the polymerization, the rate of heat generation, and the properties and the morphology of the polymer latex particles. It also makes it possible to achieve relatively high polymer quality such as homogeneous chemical composition and particle size distribution.

The semi-continuous emulsion polymerization processes is characterized by continued addition of reaction ingredients such as monomer, emulsifier, initiator, or water to the reaction system throughout the polymerization. In this emulsion polymerization process, two major types of feeds are used for the introduction of ingredients to the reactor; neat monomer feed or monomer emulsion feed. In neat monomer feed method, the feed contains only monomer and all the other ingredients are initially in the reactor. Otherwise, the major components of the monomer emulsion feed are a monomer, a part from the emulsifier, and water. But it contains other ingredients. The main difference between the two types is the emulsifier concentration throughout the polymerization. The initiator can initially be charged or/and continuously fed during polymerization. By the continuous addition of the emulsifier, monomer, and initiator to the reaction mixture, the mechanisms (especially particle formation) and kinetics of the semi-continuous emulsion polymerization process become more complicated in comparison with the batch counterpart.

A semi-continuous process generally contains three successive operations: seeding batch stage (or preliminary batch), feed addition semi-continuous stage and finishing batch stage. Generally, a semi-continuous process starts with a seeding batch stage which is the most critical stage of a semi-continuous process. It controls the particle formation in the whole course of the reaction. Therefore, the distributions of ingredients between initial reactor charge and feed have a great effect on the particle formation. The time interval between initiation and the start of feeding, which is called the "pre-period" or "seeding time", will determine the duration of seeding batch. Further growth of polymer particles is achieved by absorption of the monomer from the feed. After the pre-period time, particle nucleation may be complete but, in some conditions, nucleation can continue during the feeding period. If no pre-period is allowed, the seeding proceeds during the feed addition stage. The feeding stage is generally known as the "growth stage" and is the only stage within the three stages defined above which is carried out semi-continuous wise. The finishing batch is carried out to reduce the amount of unreacted monomer remaining in the reaction mixture to a minimum [48-50].

Consequently, semi-continuous emulsion polymerization is an important process, which overcomes the disadvantages of the batch and continuous processes, for the

manufacture of a variety of latex products because of its operational flexibility and, providing control on the polymerization and the properties of polymer and latex.

In continuous process, the reaction system is continuously fed to, and removed from, a suitable reactor at rates such that the total volume of system undergoing reaction at any instant is constant. Generally, conversion and particle number are lower and the particle size distribution is broader as compared to batch process. In particular, the particle nucleation stage is sensitive to residence time distribution [31,47,51]. Continuous emulsion polymerization process is useful for the production of commercial latexes. This process enables economical production of large volume, formation a highly uniform and well regulated product, and fewer problems with wall polymer buildup and coagulation. But, it allows less operational flexibility and less control on the product characteristics such as specific particle size distribution or particle morphologies [32].

## 2.2 Graft Copolymerization

Polymers which contain more than one type of structural unit are called as copolymers. The copolymer with random distribution of the different mers or repeating units in its structure is commonly referred to as a random copolymer. In the alternating copolymer the two mers alternate in a regular fashion along the polymer chain. A block copolymer is a linear polymer with one or more long uninterrupted sequence of each mer in the chain. A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points (Figure 2.3).

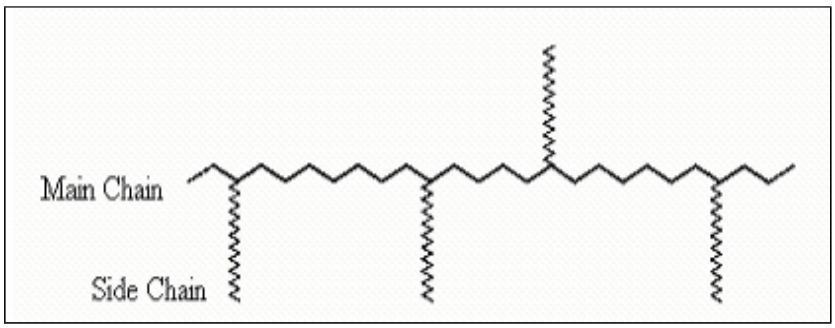


**Figure 2.3:** Graft copolymer

It can be generally carried out by abstraction of hydrogen atoms from the polymeric back- bone by chemical methods using processes in bulk [52], solution [53], emulsion [54], or miniemulsion [55], via borane compounds [56] and in supercritical conditions ($CO_2$) [57], by gamma irradiations ($\gamma$) [58], ultraviolet (UV) irradiation [59], electron beam [60], or plasma [61], and by mechanical methods using high shear rate: reactive extrusion and mixing chamber [62], in the presence or absence of a peroxide-type initiator or azo-compounds; and using diverse commercial monomers or macromonomers previously synthesized.

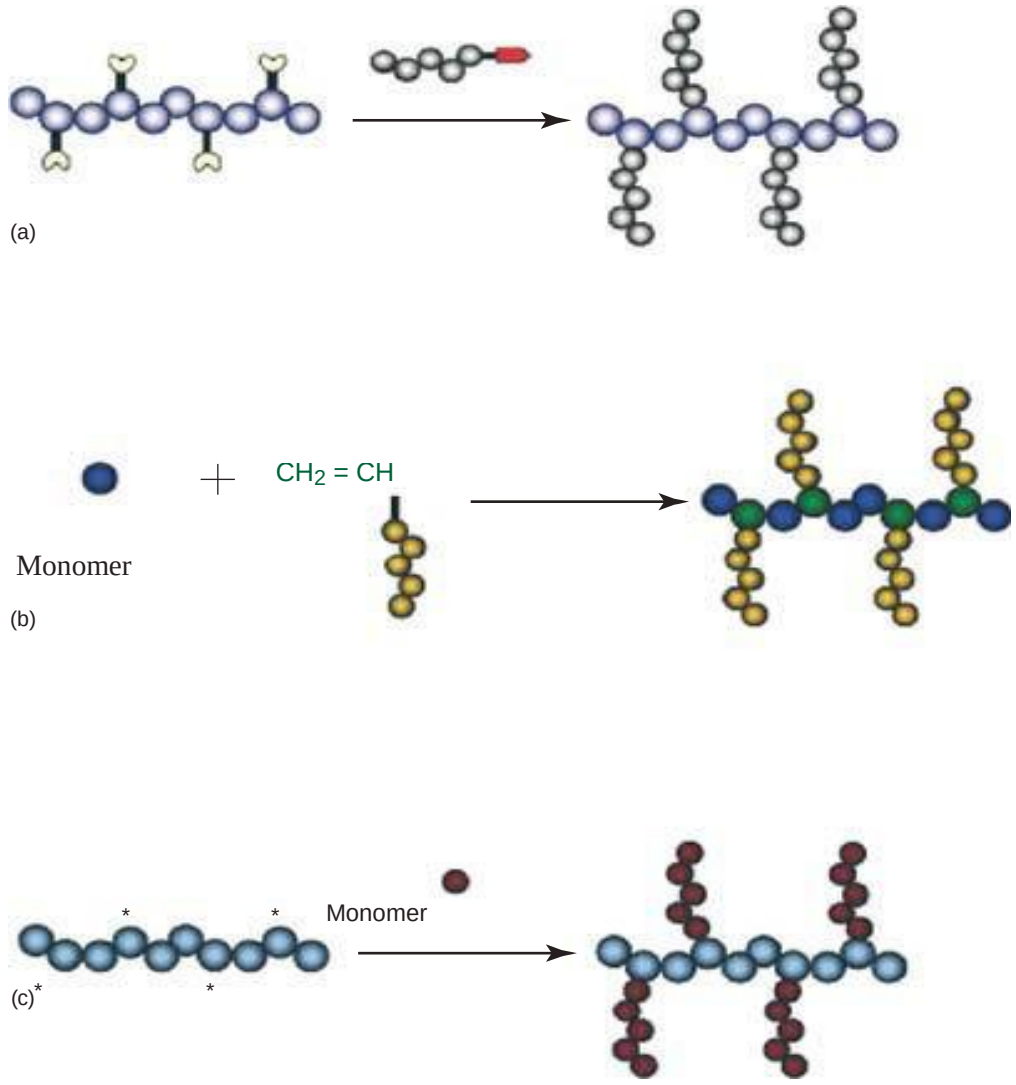


**Figure 2.4:** Schematic representation of (a) grafting-onto, (b) grafting through, and (c) grafting-from methods

Graft copolymers represent valuable polymeric materials, since a variety of molecular parameters can be varied:

i) Main and side chain polymer type,

ii) Degree of polymerization and polydispersities of main and side chain,

iii) Graft density (average spacing in-between the side chains),

iv) Distribution of the grafts (graft uniformity).

Using special polymerization techniques tailor-made graft copolymers can be afforded according to specific needs. By controlling the molecular parameters, one can obtain impact resistant materials, by combining a hard polymer backbone with soft polymer side chains; thermoplastic elastomers, whereas of polymer backbone is grafted with hard polymer segments; or amphiphilic copolymers for applications as hydrogels, stabilizers, surface-modifying agents, dispersants and compatibilizers in polymer blends [63,64].

Three main methods can be used to prepare graft copolymers: i) "grafting through", where a macromonomer is copolymerized with a low molecular weight comonomer; ii) "grafting from"; in this case a macro initiator with predetermined initiation sides is used to initiate the polymerization of a second monomer; iii) "grafting onto", where an end-functional or a living polymer with reactive end-group is coupled with functional groups located on another polymer (Figure 2.4).

### 2.2.1 Graft copolymers by the "grafting through" approach

The "grafting through" approach is the most common route to controlled graft copolymers [65,66]. The "grafting-through" method uses macromonomers (polymer chains of very low molecular weight or oligomers) containing groups at their end that are capable of carrying out polymerization, particularly vinyl groups. The avarage side chain density is determined by their activity ratio of the macromonomer in the copolymerization and by the ratio of the macromonomer in the feed. The spacing distribution of the side chains is the most crucial parameter to control. It is influenced by the diffusion differences of in acromonomer comparison to the low molecular weight comonomer [67], by the inherent reactivity of macromonomer and comonomer [68] and by the potential in compatibility of the side chain polymer with the main chain polymer [69]. The addition of a second monomer (comonomer) in the presence or absence (in the case of auto-initiation) of an initiator, leads to the construction of several complex topologies of graft copolymers. Indeed, depending

of the reactivity ratios and the distance between adjacent grafts, brushes, regular grafts, centipede, barbwire, etc., structures can be produced [70].

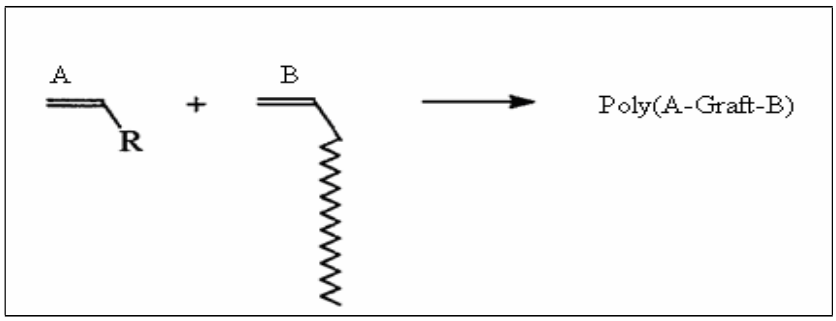


**Figure 2.5:** Grafting through approach

### 2.2.2 Graft copolymers by the "grafting from" approach

It is the synthesis *in situ* of grafts of homopolymers or copolymers (small or long chains) containing functional groups, starting from units located along an existing polymer backbone. "Grafting-from" is the most popular method used to obtain graft polymers, and requires a polymer containing reactive groups, functional species or initiator moieties along its backbone, which in the presence of monomers, produce the growth of grafts from the surface of the substrate [71-73]. Thus, the number of grafts can be controlled by the number of actives sites present along the backbone.

This approach uses a macroinitiator that carries initiation groups to start a polymerization reaction of a monomer. The synthesis of the macroinitiator allows the control of the main chain parameters (DP, $M_W/M_n$) as well as the pre-determination of side chain density and side chain distribution. The main difficulty in this approach is to ensure a uniform propagation of the side chains and furthermore to suppress chain coupling reactions. The method is not restricted to linear macroinitiator, particles [74,75] and surfaces [76,77] are also succesfully functionalized with initiating groups and used as macroinitiator to get access to e.g. inorganic/organic hybrid materials.

Using "grafting through" and "grafting from" methods, the molecular parameters such as the degree of polymerization of and as the degree of polymerization of and the polydispersity of main and side chain polymer, graft density and graft distribution could be controlled.

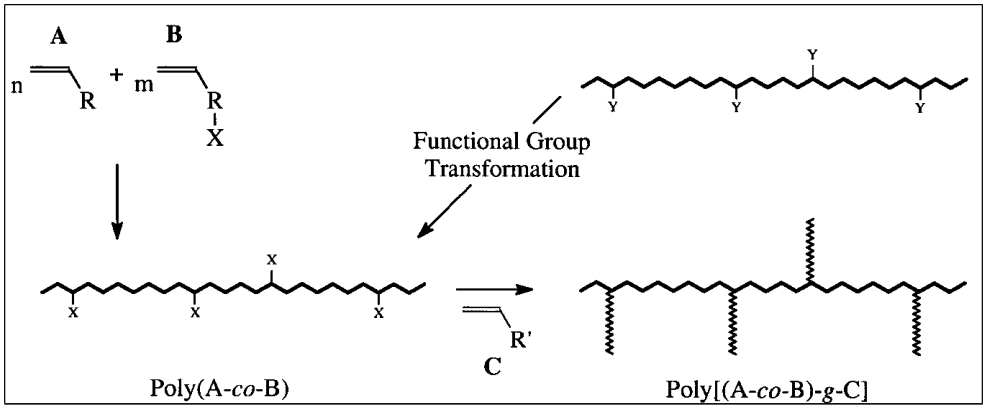


**Figure 2.6:** Grafting from approach

### 2.2.3 Graft copolymers by the "grafting onto" approach

This technique, "grafting-onto" (also called *grafting- to*), involves the reaction of an end-functional structure previously synthesized with a complementary functional monomeric unit present in the polymer backbone. Thus, grafting-onto is widely used for the synthesis of comb polymers.

## 2.3 Natural Rubber

Natural rubber (NR) has been known to the civilised world ever since the year 1493, when Christopher Columbus found the natives of Haiti playing with balls made from the exudates of a tree called 'cau-uchu' or weeping wood. The term 'rubber' was coined by the English chemist Joseph Priestly for its ability to erase pencil marks. It was the French scientist Charles de la Condamine who first introduced NR to Europe in 1736 and published his observations in 1745. Industrial applications of rubber were found slowly after this. It was the discovery of vulcanisation by Charles Goodyear in 1839 that paved the way for the growth of the modern rubber industry [78].

Natural rubber is cis-1, 4 polyisoprene and is present as latex in a large variety of plants in many regions of the world. Latex containing appreciable quantities of rubber occurs in certain plant species belonging to the *Moraceae, Euphorbiaceae, Apocynaceae* and *Compositae* families. *Hevea brasiliensis*, the most widely exploited commercial source of NR, was introduced into tropical Asia in 1876 by Sir Henry Wickham.

The limited availability of petroleum-based feed stocks and the increasing awareness of the relevance of renewable and environment- friendly resources such as NR, have caused renewed interest in the development of modified forms of NR [79,80].

### 2.3.1 Modification of Natural Rubber

Natural rubber can be modified by physical and/or chemical means [79]. Figure 2.7 gives an outline of the major modifications of NR.

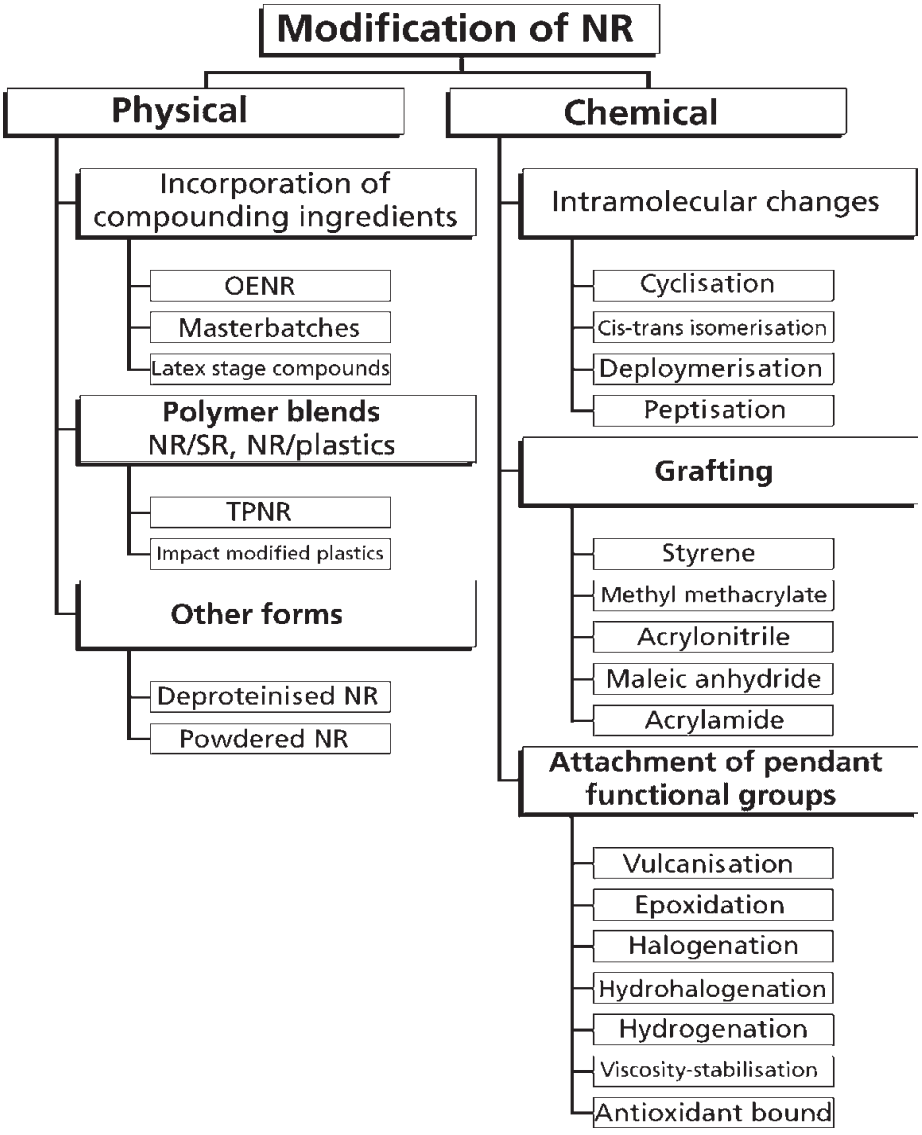


**Figure 2.7:** Modification of natural rubber [79]

Some of these such as viscosity stabilised rubber, superior processing rubber, have been produced commercially. The commercial significance of the others depends mostly on emerging market forces.

#### 2.3.1.1 Physically Modified Forms of Natural Rubber

The physical methods of modification of NR involve incorporation of additives which do not chemically react with rubber.

The additives include various rubber compounding ingredients and polymers such as synthetic rubbers and thermoplastics [79]. Some of the commercially important materials in this group are

a) Oil extended natural rubber (OENR)

b) Thermoplastic natural rubber (TPNR)

c) Deproteinised natural rubber (DPNR)

#### 2.3.1.2 Chemically Modified Forms of Natural Rubber

Being an unsaturated organic compound, natural rubber is highly reactive and several chemical reactions can be carried out in NR resulting in materials having entirely different properties [79]. These reactions can take place by the attachment of pendant functional groups, grafting of different polymers along the rubber molecule or through intra-molecular changes.

The products of the reactions possess properties which are different from those of NR and therefore, can find use in applications where other materials are being used. Some of the important chemically modified forms of NR are

a) Constant viscosity (CV) rubber

b) Graft copolymer rubbers

c) Epoxidised natural rubber (ENR)

d) Superior processing (SP) rubber

### 2.3.2 Properties of natural rubber

Natural rubber is a high molecular weight polymer having the chemical structure, cis- 1, 4 polyisoprene. The raw rubber contains, in addition to the rubber hydrocarbon, small quantities of proteins, fats, fatty acids, carbohydrates, mineral matter. The rubber hydrocarbon content is about 94%. The physical and chemical properties of the rubber are influenced by the presence of the non-rubber substances.

Being a linear long chain polymer, NR is composed of molecules of different sizes. The weight average molecular weight (Mw) of NR ranges from 30,000 to about 10 million. A random blend would have an Mw of about 2 x 106 and a number average weight (Mn) of 5 x 105. Subramaniam [81] demonstrated that the molecular weight distribution (MWD) of unmasticated NR is distinctly bimodal. The clonal variation in molecular weight and MWD was also studied by Subramaniam [82]. A small portion of the rubber undergoes crosslinking even in the latex present within the latex vessels of the tree. The usual concentration of this microgel is 7–30% and influences the melt viscosity of the rubber. The gel content of raw NR which has been stored for some time is much higher and is known as macrogel, and is responsible for the increased viscosity during storage. The presence of certain active chemical groups such as carbonyl groups on the rubber chain is believed to cause formation of branched chains. Mastication reduces the gel content. The rheological properties of NR are strongly influenced by long chain branching. The slow rate of stress relaxation of Hevea rubber compared to guayule and synthetic polyisoprene rubber has been attributed to chain branching [83].

Storage of NR at subzero temperatures causes stiffening of the rubber and the maximum rate of crystallization occurs at –24 $^0$C. Such stiffened rubber requires thawing at 40–50 $^0$C before processing. The temperature at which the last traces of crystallinity disappears is described as the melting temperature, $T_m$. Although a value of 28 $^0$C has been assigned for the $T_m$ of NR, values of 30 $^0$C and higher depending on storage temperature and duration, have been occasionally reported.

All polymeric materials will, at some temperature, undergo a glass transition ($T_g$), and change from a glassy to a rubbery state. Specific volume measurements on NR have established a $T_g$ of –72 $^0$C. While carbon black has relatively little influence on $T_g$ of NR, plasticizers depress it considerably and crosslinking increases it.

### 2.3.3 Processing properties of natural rubber

The processing characteristics of NR are considered to be excellent. Although it is tough and nervy at temperatures below 100 0C, it breaks down easily to a workable viscosity. The normal fabrication techniques can easily be adopted for NR. Although premastication is not required for the viscosity stabilized grades, mastication is commonly practiced for the normal grades. The efficiency of mastication is

temperature dependent and is the least at around 100 $^0$C [84,85]. Chemical peptisers allow mastication to be carried out at lower temperatures and are useful for increasing the efficiency of mastication. Rubbers with high initial viscosity tend to break down faster mostly due to the high shearing forces realized. The break down behavior also depends on the plasticity retention index (PRI) of the rubbers and it is generally found that latex grades with high PRI values break down more slowly than field coagulum grades. It is observed that because of the faster break down behavior of NR compared to SBR, the average viscosity of a NR mix during mixing is lower than that of a similar SBR mix, although the initial viscosity is much higher for NR. This leads to lower energy consumption for mixing the NR compound.

The batch viscosity is the main factor controlling die swell and the stress developed while extruding a fully mixed compound. Thus viscosity is a useful guide to assess the processing behaviour of masticated rubbers. A masticated rubber has better extrusion properties than an unmasticated rubber of the same viscosity.

The most important aspects of processability of NR are its high inherent tack and green strength. These two characteristics are of utmost importance in the manufacture of products such as tyres. Tack is important as it holds the compounds of green tyre together until moulding. Green strength is needed so that the uncured tyre will not creep and hence distort excessively before moulding or tear during the expansion that occurs upon moulding. A practical definition of tack is the ability of two similar materials to resist separation after they are brought into contact for a short time under a light pressure. The higher tack of NR compared to SBR has been attributed to its greater ability to flow under compressive load and its higher green strength. NR is an ideal material for developing high tack. It can be processed to a low viscosity and still maintain high green strength. Furthermore, the mechanism responsible for high green strength is strain crystallisation which is not active in the bond formation stage and hence does not interfere with contact and interdiffusion, but rather develops upon stretching.

# 3. EXPERIMENTAL WORK

## 3.1 Materials

The commercial high-ammonia Natural Rubber Latex (NR) with 60% by weight dry rubber content. It was manufactured and supplied by Thai Hua Rubber Public Company Ltd. and was used as received. Styrene (St, 99,97%; Vitsan), sodium lauryl sulfate as anionic emulsifier (SLS, $CH_3(CH_2)_{11}OSO_3Na$; Cognis), fatty alcohol ethoxylate as nonionic emulsifier (30 EO, 70% active content; BASF), sodium salt of alkyl ether sulphate as anionic emulsifier (7 EO, 30% active content; Clariant), potassium hydroxide (KOH, 91%; Ercros), sodium bicarbonate ($NaHCO_3$; Eti Soda), ammonium persulfate (APS, $(NH_4)_2S_2O_8$; Acar Chemicals), calcium chloride ($CaCl_2$; Weifang Qiangyuan Chemical) were used as received. Light petroleum ether (60-80 $^oC$ bp; Merck), ethyl methyl ketone (>99%; Merck), acetone (>99.8%; Sigma-Aldrich) were used as received. Distilled water was used throughout the work.

## 3.2 Instrumentation

$^1$H-NMR spectra were recorded on an Agilent VNMRS 500 (500 MHz for proton and 125 MHz for carbon) and on a Bruker AC-250 spectrometer (250 MHz for proton). FT-IR spectra were recorded on Perkin Elmer Spectrum One FT-IR instrument. The amount of residual monomer was determined with an Agilent Model 6890N Network GC System. The number-average diameter of the particles was measured using dynamic light scattering technique on Malvern Mastersizer 2000. Weatherability was tested in the Q-Lab QUV Accelerated Weathering Tester.

## 3.3 Synthesis Procedure of Graft Copolymerization of Styrene onto Natural Rubber

The graft copolymerization reaction of St with NR was carried out in a 1000-ml four

necked, round-bottomed flask equipped with stirrer, thermometer, reflux condenser, and gas inlet tube. Distilled water, 9.3 g SLS as emulsifier, and 344.3 g NR were charged to the reactor. 2.06 g $NaHCO_3$ and 0.83 g KOH were added as buffer and to maintain the pH of the latex at approximately 10, respectively. Then, the dissolved oxygen in the ingredients was removed by purging with nitrogen gas for least 30 min through the mixture, while continuously providing stable latex. 46.98 g of 10% aqueous solution of APS as thermal initiator was prepared. The monomer emulsion consisting of totally 3.49 grams of anionic emulsifier and nonionic emulsifier, deionized water and 77.66 g St was incorporated into a feeding tank and subsequently added drop-wise into the main reactor for 4 hours at 85 $^0$C. The one-third of initiator was fed in 15 minutes and the remaining was dosaged for 3.45 h. After the completion of dosing, the reaction was stirred another 1 h. The polymerization reaction was performed with a stirring speed of 300 rpm.

$^1$H NMR ($CDCl_3$, δ) 7.27 (s, 3H), 7.05 (m, 5H), 5.13 (s, 2H), 3.75 (t, 8H), 2.04 (s, 2H), 1.86 (p, 8H), 1.68 (s, 6H), 1.26 (s, 1H).

## 4. RESULTS AND DISCUSSION

Natural rubber is a renewable resourced polymer with perfect mechanical strength. Due to its high tensile strength and resilience properties, it is commonly used in carpet-back coating. On the other hand, unsaturated carbon double bonds make it weak in weather resistance. Hence, it is seen that after a while the coating becomes sticky or even degraded.

In this study, the hard St monomer was grafted onto NR to improve heat and UV resistance while maintaining its mechanical properties. Research on graft copolymerization of NR has been done for many years [2,13,20-24]. The distinguishing feature of this study is its application in carpet industry. Furthermore, low cost thermal initiator was effectively used to initiate the copolymerization. The successful results of coating practice of St-*g*-NR made it a commercial product.

The graft copolymerization of St onto NR was performed by emulsion polymerization method. It was an exothermic reaction. The reaction temperature was easier controlled because of more rapid heat transfer in the low viscosity emulsion. It was $\pm 2\ ^{0}C$ around the reaction temperature during polymerization.

Surfactants reduce surface tension of water until a specific concentration, which is critical micelle concentration. Micelles in which polymerization occurs develop above this point. Therefore, the concentration should be determined appropriately to obtain higher conversion rate. The type of surfactant used in emulsion polymerization is greatly important. Anionic surfactants generate strong particles and stabilize them via electrostatic repulsion mechanism. However, these are weak to electrolytes. To eliminate this problem, nonionic surfactants can be used to nucleate and to provide steric stabilization against electrolytes, freeze-thaw cycles. So, nonionic/anionic surfactant combination, fatty alcohol ethoxylate and sodium lauryl sulfate were used in the synthesis of St-*g*-NR to control the particle size and to enhance colloidal stability [39-41].

Emulsion polymerization occurs following the radical mechanism. The formation of free radicals can be obtained by redox or thermal initiators. Due to low reaction temperature requirement, redox initiators have been preferred in many studies of graft copolymerizations of NR [1,3,15]. On the other hand, ammonium persulfate, thermal initiator was used in the synthesis of St-*g*-NR because of its cost effectiveness and less risk of damage to health. Free radicals were produced by breakage of a single bond via heat. These radicals created active centers on NR chain. Polymer enlarged by the addition of St monomers to the active centers as shown in Figure 4.1.

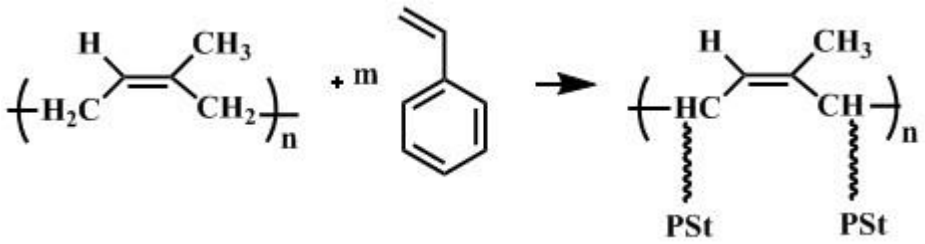


**Figure 4.1:** Schematic representation of graft copolymerization of St onto natural rubber

The graft copolymer was prepared using a weight ratio of NR/St at 82/18. In this study, the effect of initiator concentration and reaction temperature on free radical graft copolymerization of St onto NR was investigated.

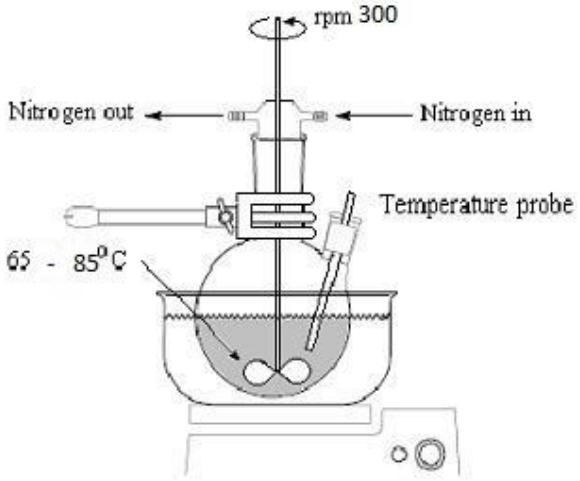


**Figure 4.2:** Laboratory scale apparatus used to prepare St-*g*-NR

First of all, the initiation concentration was fixed for temperature investigation at 0,5 mol/L. The reaction temperatures were varied at 65, 75, and 85 $^{0}$C. The results of conversion, % free natural rubber, % free polystyrene, and grafting efficiency were summarized in Table 4.1.

**Table 4.1:** Effect of polymerization temperature on the graft efficiency at 0,5 mol/L initiator concentration.

| | **Reaction Temperature (ºC)** | **% Free Natural Rubber** | **% Free Polystyrene** | **% Grafting Efficiency** |
|---|---|---|---|---|
| **VP9** | 65 | 11.7 | 20.1 | 51.1 |
| **VP7** | 75 | 10.1 | 20.6 | 53.9 |
| **VP8** | 85 | 13.4 | 17.4 | 59.2 |

The results indicate that the grafting efficiency increases as the polymerization temperature is increased. The rate of decomposition of the initiator depends on the reaction temperature. More sulfate radicals are produced with an increase in reaction temperature. It is also known that the transfer of these sulfate radicals to the rubber chain produces the graft copolymers.

In the second part, the effect of the amount of initiator on the grafting efficiency was studied over the range of approximately 0,1 to 1,0 mol/L while keeping the concentration of all other reagents and the reaction tempertaure, 85 $^{0}$C. The results established that the grafting efficiency raised with an increase in the amount of initiator from 0,1 to 1,0 mol/L (Table 4.2). This trend can be explained by the fact that the radicals produce macroradicals by transferring to either rubber of monomer, consequently resulting in an increase in grafting.

**Table 4.2:** Effect of initiator concentration on the graft efficiency at 85 $^{0}$C polymerization temperature.

| | **Initiator Concentration (mol/L)** | **% Free Natural Rubber** | **% Free Polystyrene** | **% Grafting Efficiency** |
|---|---|---|---|---|
| **VP11** | 0,1 | 13,2 | 23,9 | 47,5 |
| **VP8** | 0,5 | 13,4 | 17,4 | 59,2 |
| **VP10** | 1,0 | 8,3 | 7,4 | 75,9 |

The reaction products in latex form were analyzed by Gas Chromatography to detect the amount of residual monomer. The results pointed out the conversion rate of St monomer in reaction as seen in Table 4.3.

**Table 4.3:** Conversion rate of graft copolymerization

| | **VP7** | **VP8** | **VP9** | **VP10** | **VP11** |
|---|---|---|---|---|---|
| **Conversion (%)** | 99.95 | 99.96 | 99.89 | 99.97 | 97.89 |

By compilation of Table 4.1, Table 4.2, and Table 4.3, it is seen that the conversion rates of VP7, VP8, VP9, and VP10 are almost the same. However, the rate of grafted St grows by the effect of polymerization temperature and initiator concentration. In conclusion, the highest grafting efficiency was obtained at VP10.

The amount of unreacted NR, free homopolymer and St-*g*-NR in the reaction products were determined by Soxhlet extraction. A small amount of copolymer was sampled for analysis. The latex sample was coagulated with a 10% aqueous solution of $CaCl_2$, then washed with distilled water to remove any water-soluble impurities from the rubber, and finally dried at 40 $^0$C. Soxhlet extraction procedures were carried out to assess the amounts of free NR and free PSt in the graft copolymer.

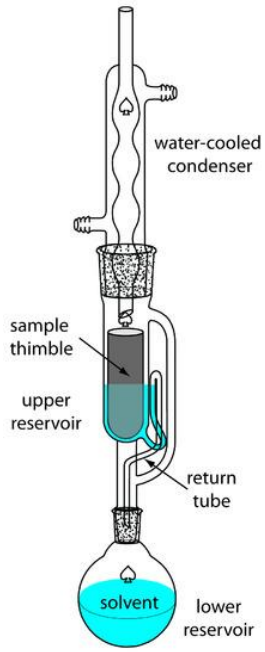


**Figure 4.3:** The Soxhlet extraction apparatus

Firstly, the free NR was extracted with 60-80 $^0$C boiling point petroleum ether for 24 hours. The remaining product was dried in an oven at 40 $^0$C for 24 hours. To remove the free PSt, the residue was further extracted in ether methyl ketone: acetone (50:50, v/v) mixture at 80 $^0$C for 24 hours and again dried in an oven to a constant weight at 40 $^o$C. By the weights of extracts and residue, the grafting efficiency, the percentage of free PSt (FP), and the percentage of grafted natural rubber (GNR) were calculated using the following relationships:

$$\text{Graft efficiency} = \frac{\text{weight (g) of graft-polymerized monomers}}{\text{weight (g) of total polymerized monomers}} \times 100$$

$$\text{FP (\%)} = \frac{\text{weight of free copolymers}}{\text{weight of the gross polymers}} \times 100$$

$$\text{GNR (\%)} = \frac{\text{weight of graft copolymers}}{\text{weight of the gross polymers}} \times 100$$

The purified St-*g*-NR was analyzed for its functional groups by FTIR and NMR techniques. The free natural rubber (FNR) was also analyzed in order to compare the results.

The 5-10% (w/v) solution of FNR and St-*g*-NR samples in deuterated chloroform ($CDCl_3$) were characterized with $^1$H-NMR. The NMR spectra are shown in Figure 4.4 and Figure 4.5, respectively. The signal of aromatic protons of PSt at the chemical shifts of 6.5-7.5 ppm, the signal of aliphatic =CH protons of polyisoprene at about 5.1 ppm, and the signal of aliphatic protons of the alkene at about 1-2 ppm were clearly observed. This confirms the occurrence of grafting polymerization of St onto NR.

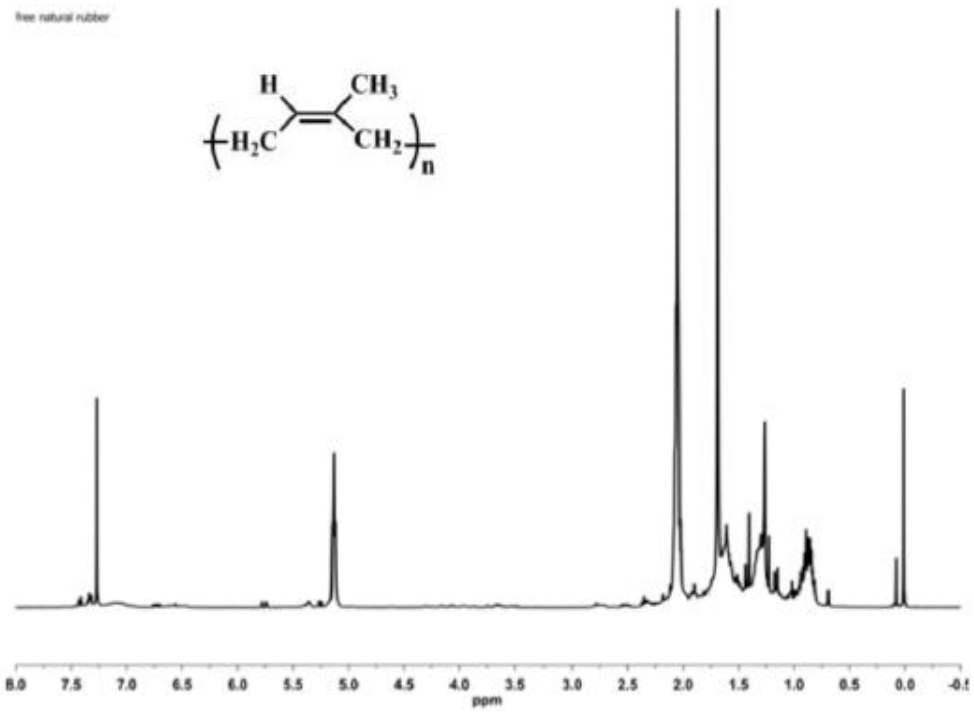


**Figure 4.4:** $^1$H NMR spectrum of FNR

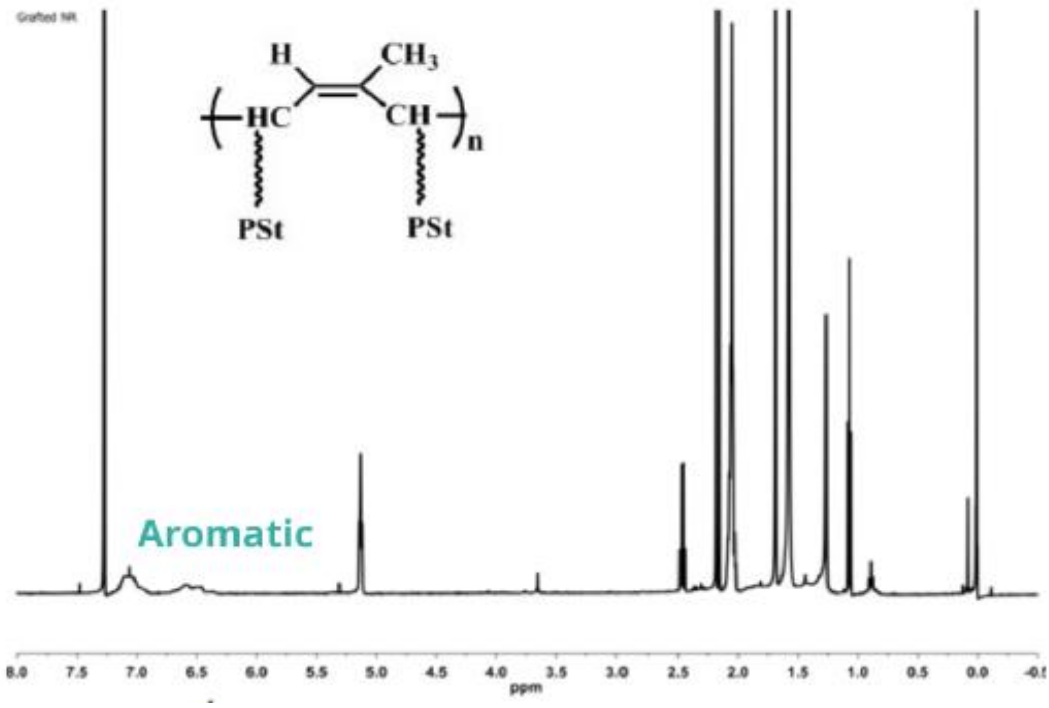


**Figure 4.5:** $^{1}$H NMR spectrum of St-*g*-NR of VP7

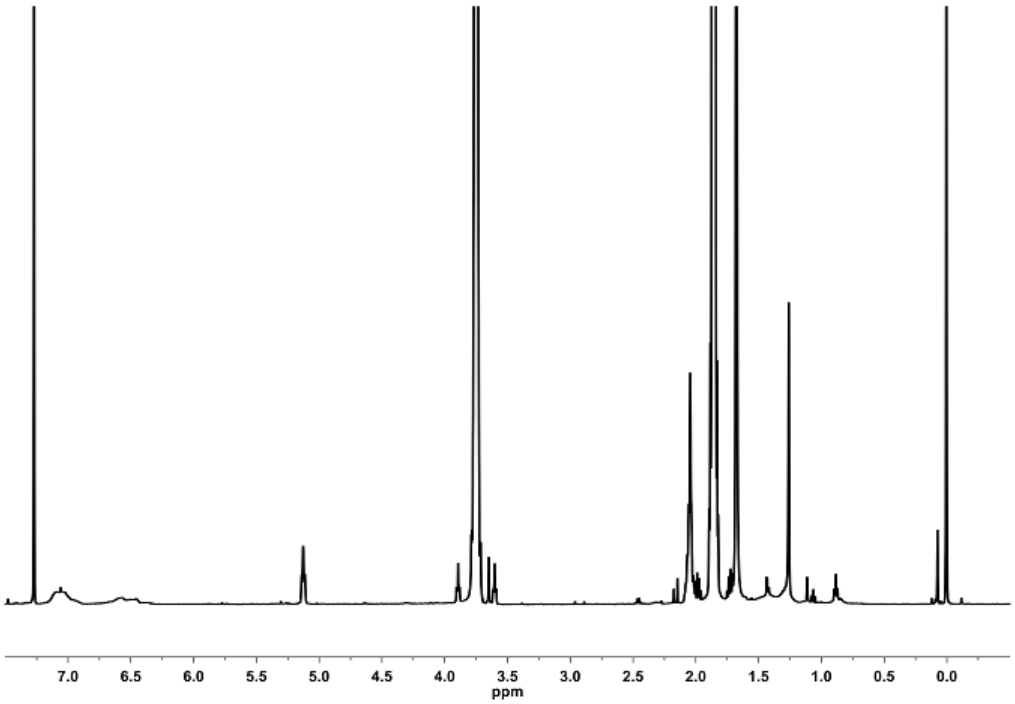


**Figure 4.6:** $^{1}$H NMR spectrum of St-*g*-NR of VP8

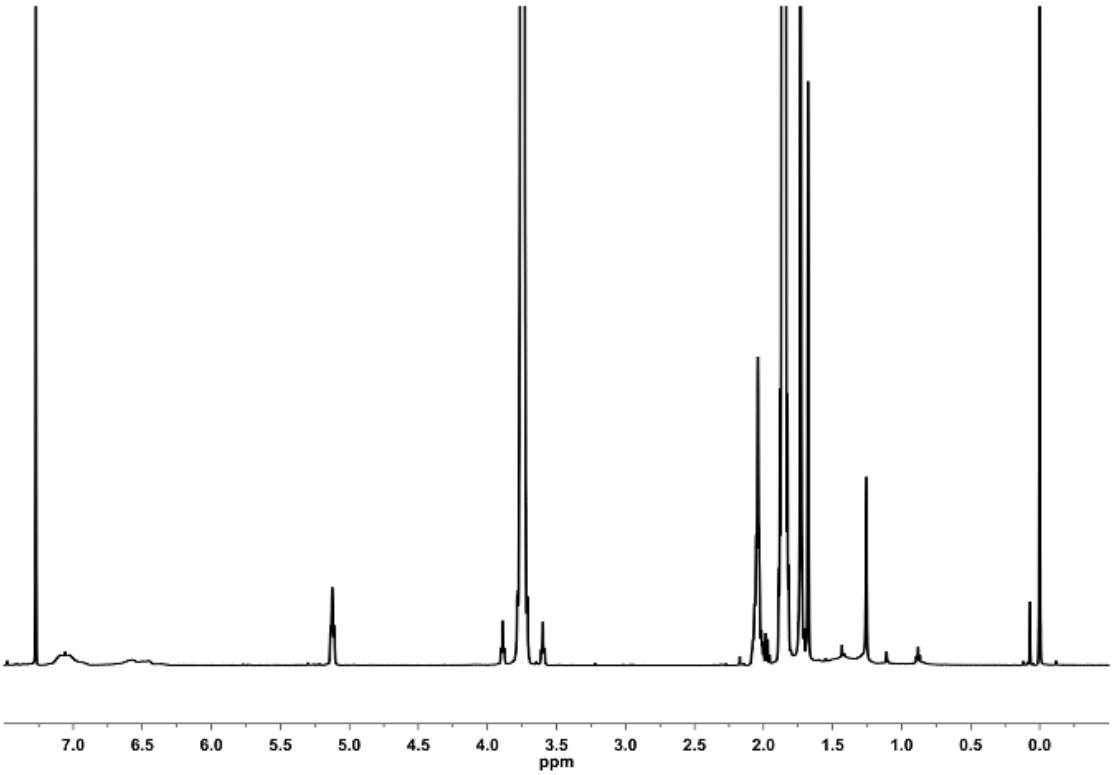


**Figure 4.7:** $^{1}$H NMR spectrum of St-*g*-NR of VP9

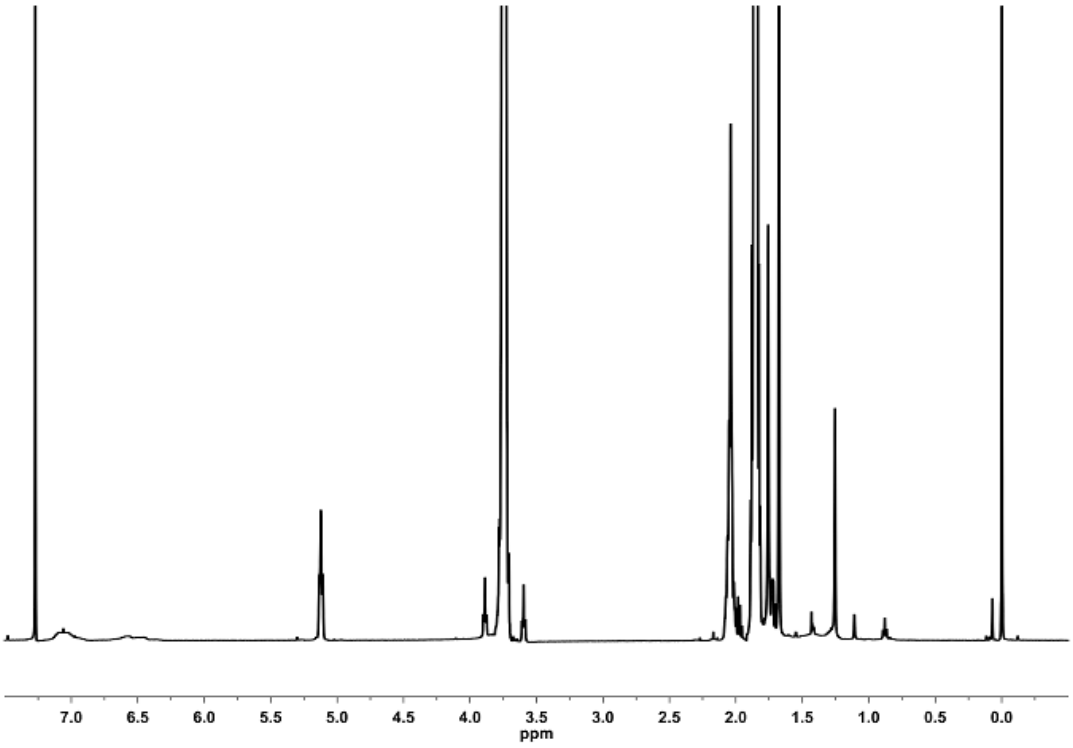


**Figure 4.8:** $^{1}$H NMR spectrum of St-*g*-NR of VP10

The FTIR spectra of FNR and St-*g*-NR are shown in Figure 4.9 and Figure 4.10, respectively. The absorption peaks at the wavenumbers of 836, and 1634 $cm^{-1}$ in the free natural rubber molecule are specific peaks of NR belonging =C-H, C=C stretching, respectively. The 699 $cm^{-1}$ peak in Figure 4.10 corresponds to the bending aromatic C-H of St, and 2960 $cm^{-1}$ peak arises from the aromatic CH stretching ring. The result clearly shows the existence of grafting polymerization of St onto NR.

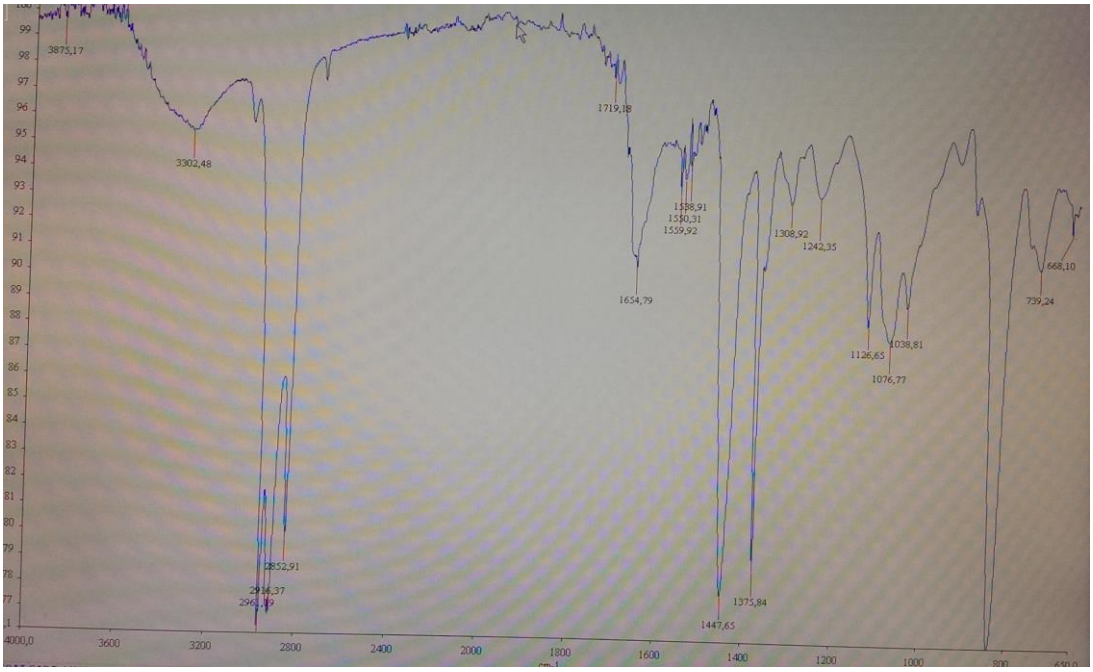


**Figure 4.9:** FTIR spectrum of FNR

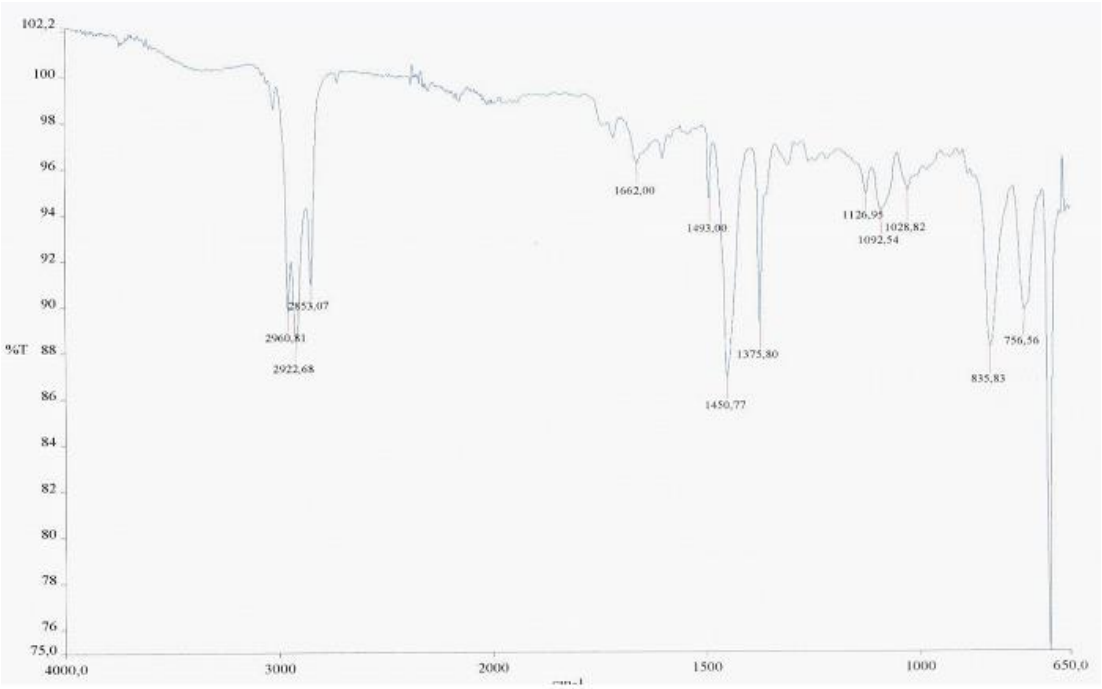


**Figure 4.10:** FTIR spectrum of St-*g*-NR of VP7

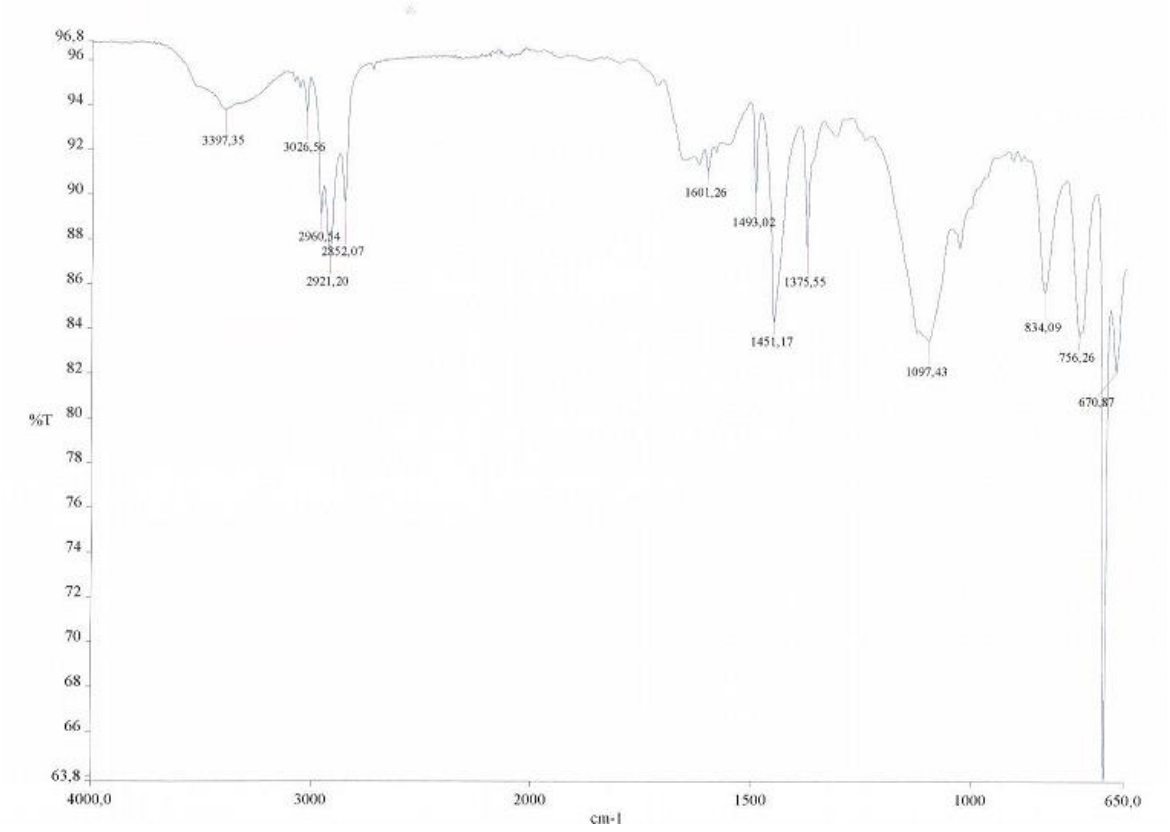


**Figure 4.11:** FTIR spectrum of St-*g*-NR of VP8

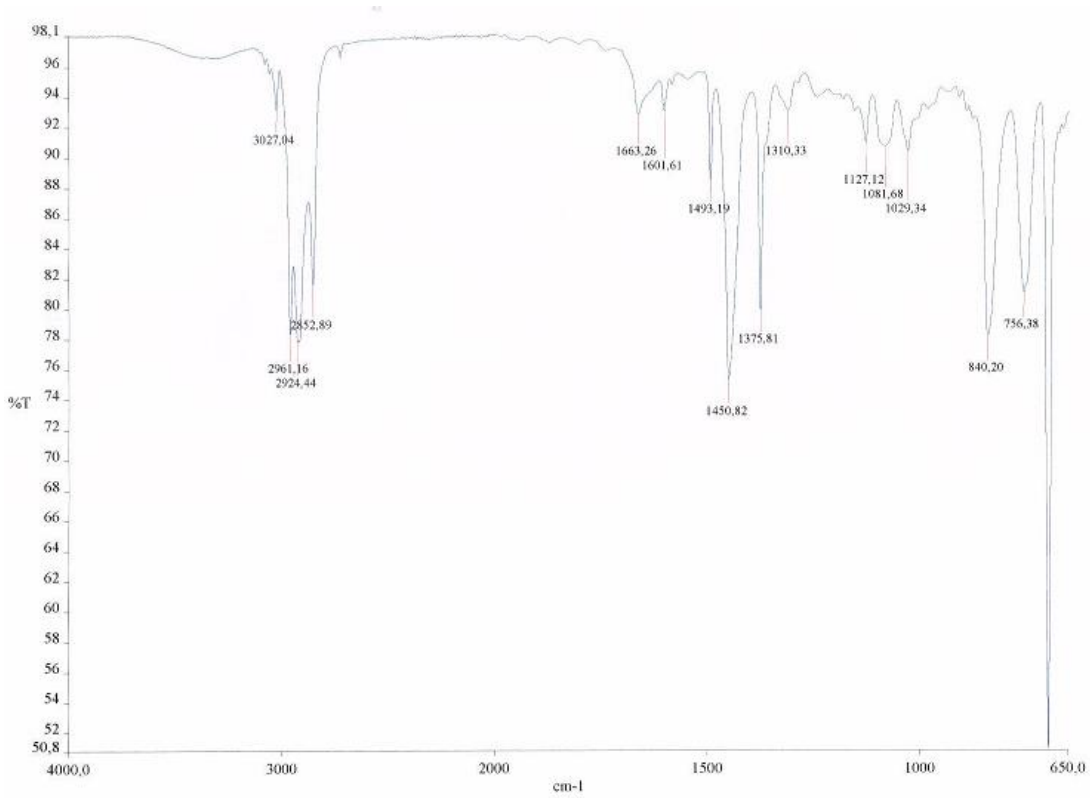


**Figure 4.12:** FTIR spectrum of St-*g*-NR of VP9

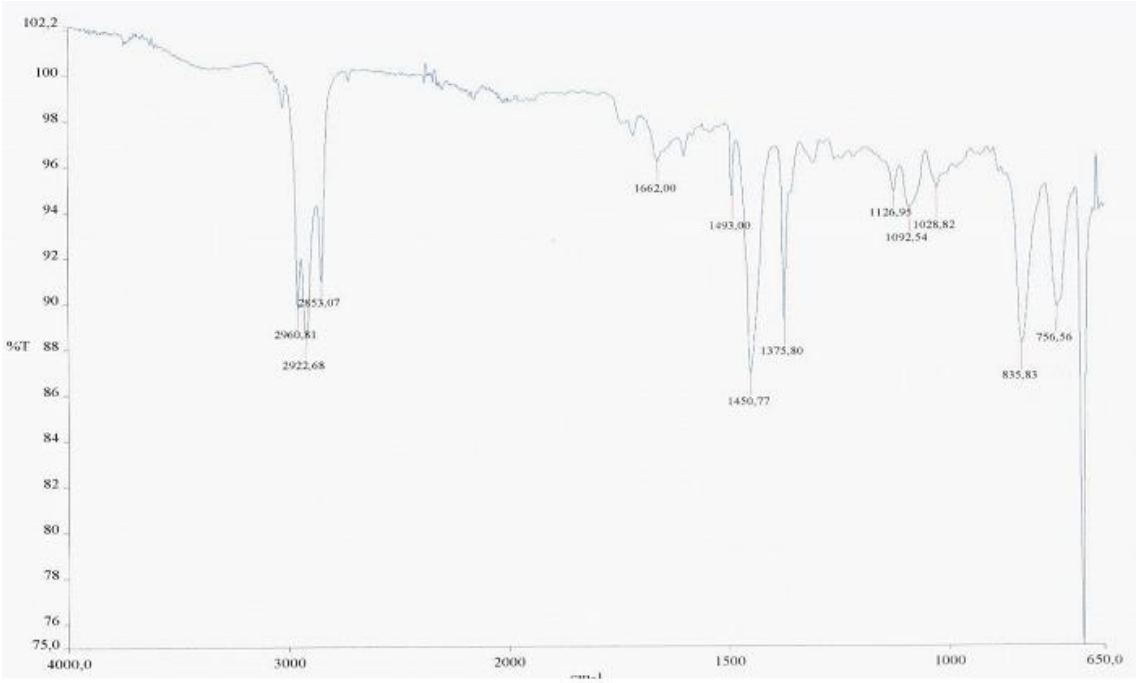


**Figure 4.13:** FTIR spectrum of St-*g*-NR of VP10

It is known that the grafting of St onto NR particles occurs mainly at the interface and the particle sizes of NR increase after copolymerization. The investigation of St-*g*-NR particle sizes by Dynamic Light Scattering technique clearly showed that average size of these particles increased at the end of the copolymerization reaction.

**Table 4.4:** Particle size of graft copolymers

| **Particle Size (um)** | **Free NR** | **VP7** | **VP8** | **VP9** | **VP10** | **VP11** |
|---|---|---|---|---|---|---|
| **d (0.1)** | 0.114 | 0.241 | 0.102 | 0.392 | 0.344 | 0.367 |
| **d (0.5)** | 0.517 | 0.798 | 0.640 | 681.07 | 0.757 | 0.722 |
| **d (0.9)** | 1.463 | 1.646 | 1.794 | 1331.84 | 1.623 | 1.392 |

For comparison of weathering resistance of St-*g*-NR and NR latex were tested together in Q-UV Accelerated Weathering test equipment. The 80 g/m$^2$ amount of both samples were coated on carpet back. And then they were exposed to alternating cycles of light using an UV lamp with 315 nm wavelength and 0,63 W/(m$^2$ nm) intensity at 60 $^0$C/4 h, and moisture, condensation in the dark at 50 $^0$C/4 h according to ASTM G154-00a Standard Practice for Operating Fluorescent Ultraviolet Lamp Apparatus for Exposure of Nonmetallic Materials.

The test results indicated that the weathering resistance of St-*g*-NR is much better than NR, and the St-*g*-NR coating did not become sticky like NR coating after exposure to UV and heat. Moreover, the antislip property of St-*g*-NR coating was almost as good as NR coating.

NR is much preferred product in carpet back-coatings through its mechanical strength and antislip feature. On the other hand, some post-treatment techniques are implemented in order to eliminate the problems caused by weak heat and weathering resistance. Vulcanization method is one of these treatments which has less advantages than chemical modification of NR. Copolymerization reaction does not require any harmful chemical out of monomer. However, sulphur and some additives such as activators, retarders, antidegradants, and stabilizers, dangerous to environment and human health are needed in vulcanization process. While any additional equipment is necessary for grafting method, vulcanizing machine is required for the latter method. Therefore, the synthesized graft copolymer may be a commercially competitive product by force of easy and low-cost manufacturability, mechanical strength, improved weathering resistance, and feasible results of carpet back-coating. This coating application is unique because it has not taken part in literature before.

In order to raise the conversion rate and the grafting efficiency, additional post-treatment techniques will be implemented in further studies.

## 5. CONCLUSION

The graft copolymerization of St onto NR prepared by emulsion polymerization by thermal initiator, ammonium persulfate (APS) to initiate the graft copolymerization. The influential factors of the initiator concentration, and reaction temperature were examined to compare the grafting efficiency. The graft copolymerization reaction studied with 1.0 mol/L of initiator concentration at 85 $^{0}$C gave the highest percentage grafting efficiency and percentage of grafted natural rubber. The St-*g*-NR supplied enhanced weathering resistance to NR. Consequently, the resulted product was applied as carpet back-coating to bind of piles on the back, and also providing antisilip effect. It has been developed as a commercial product.

## REFERENCES


[1] **Arayapranee W, Prasassarakich P, Rempel G. L.** (2002). Synthesis of graft copolymers from natural rubber using cumene hydroperoxide redox initiator, *Journal of Applied Polymer Science*, ***83***, 2993-3001.

[2] **Roberts A.D.** (1988). .*Natural Rubber Science and Technology; Oxford University Press: New York.*

[3] A**rayapranee W, Rempel G. L.** (2008). Morphology and mechanical properties of natural rubber and styrene-grafted natural rubber latex, *Journal of Applied Polymer Science*, ***109***, 1395-1402.

[4] **Avirah S. A, Joseph R**. (1995). Studies on natural rubber bound *para*-phenylenediamine antioxidants in NBR, *J. Appl. Polym. Sci.*, ***57,*** 1511-24.

[5] **Ismali M. N, Abd El Gaffar M. A, Shaffei K. A, Mohamed N. A.** (1999). Some novel polyamines as antioxidants for SBR vulcanizates, *Poly. Degrad. Stab.*, ***63,*** 377-83.

[6] **Zhao Y, Dan Y.** (2006). Preparation and characterization of a high molecular weight UV-stabilizer based on a derivative of 2,4-dihydrobenzophenone and its application in polymer materials, *J. Appl. Polym. Sci.*, ***102,*** 2203-11.

[7] **Poh B. T, Te C.S.** (2000). Cure index and activation energy of vulcanization of natural rubber and epoxidized natural rubber vulcanized in the presence of antioxidants, *J. Appl. Polym. Sci.*, ***77,*** 3234-8.

[8] **Ismali M. N, Yehia A.A, Korium A. A.** (2001). Evaluation of some arylphosphites as antioxidants and antifague agents in natural rubber and styrene-butadiene rubber vulcanizates, *Polym. Degrad. Stab.*, ***74***, 247-53.

[9] **Avirah S. A, Joseph R**. (1994). Studies on natural rubber-bound diphenylamine antioxidants, *Poly. Degrad. Stab.*, ***46 (2),*** 251-7.

[10] **Choi S. S.** (1998). Migration of antidegradants to the surface in NR vulcanizates: influence of content of carbon black, Bull Korean Chem. Soc., ***19 (2),*** 170-4.

[11**] Foldes E, Lohmeijer J.** (2007). Polymer/additive compatibility: study of primary antioxidants in PBD. *J. Appl. Polym. Sci.*, ***44***, 2660-2667.

[12] **Parra D.F, Freire M. T, Paoli De M. A**. (2000). Diffusion of amine stabilizers in vulcanized natural rubber compositions used in tires, *J. Appl. Polym. Sci.*, ***75***, 670-6.

[13] **Kawahara S, Kawazura T, Sawada T, Isono Y.** 2003, Preparation and characterization of natural rubber dispersed in nano-matrix, *Polymer*, **44**, 4527-31.

[14] **Brosse J. C, Campistron I, Derouet D, El Hamdaoui A, Houdayer S, Reyx D, Ritoit-Gillier S.** (2000). Chemical modifications of polydiene elastomers: A survey and some recent results, *J. Appl. Polym. Sci.*, ***78***, 1461-77.

[15] **Kochthongrasamee T, Prasassarakich P, Kiatkamjornwong S.** (2006). Effects of redox initiator on graft copolymerization of methyl methacrylate onto natural rubber, *J. Appl. Polym. Sci.*, ***101,*** 2587-2601.

[16] **Arayapranee W, Prasassarakich P, Rempel G. L.** (2003). *Journal of Applied Polymer Science*, ***89***, 63.

[17] **Pukkate N, Yamamoto Y, Kawahara S**. (2008). *Colloid Polym. Sci.*, ***286***, 411.

[18] **Okieimen F. E, Urhoghide I. N**. (1996). Studies on miscibility of poly (vinyl chloride) with natural rubber graft-polyacrylonitrile and natural rubber-graft poly (methyl methacrylate), *J. Appl. Poly. Sci.*, ***59***, 1803-1808.

[19] **Olivera P. C, Guimaraes A, Cavaille J. Y, Chazeau L, Gilbert R. G, Santos A.M.** (2005). Modification of natural rubber: A study by $^{1}$H NMR to assess the degree of graftization of polyDMAEMA or polyMMA onto natural rubber particles under latex form in the presence of a redox couple initiator, *Eur. Polym. J.*, ***41***, 1883-92.

[20] **Hammer C. F, Brandt W. W, Peticolas W. L. J.** (1957). *J. Polym. Sci.*, ***24,*** 292.

[21] **Sittiphan T, Prasassarakich P, Poompradub S. (**2013). Styrene grafted natural rubber reinforced by in situ silica generated via sol-gel technique, *Materials Science And Engineering B,* ***181,*** 39-45.

[22] **Arayapranee W, Rempel G. L.** (2003). Factorial experimental design for grafting of vinyl monomers onto natural rubber latex, *Journal of Applied Polymer Science*, ***93***, 455-463.

[23] **Asaletha R, Groeninckx G, Kumaran M. G, Thomas S.** (1998). *Journal of Applied Polymer Science*, ***69,*** 2673.

[24] **Oommen Z, Thomas S.** (1997). *J. Appl. Poly. Sci.*, ***65***, 1245.

[25] **Kalkornsurapranee E, Sahakaro K, Kaesaman A, Nakason C.** (2009). From laboratory to a pilot scale production of natural rybber grafted with PMMA, *J. Appl. Poly. Sci.*, ***114***, 587-597.

[26] **Schoonbrood H. A. S, German A. L, Gilbert R. (**1995). Rate-Determining Kinetic Mechanisms in the Seeded Emulsion Copolymerization of Styrene and Methyl Acrylate, *Macromolecules,* ***28 (1)***, 34-49.

[27] **Bovey F. A, Kolthoff I. M, Medalia A.I, Meehan, E. J.** (1965). Emulsion Polymerization, High Polymer Series, ***9***.

[28] **Blackley D.C**. (1975). Emulsion Polymerization, Theory and Practice. London: Applied Science Publishers.

[29] **Eliseeva V. I, Ivanchev S. S, Kuchanov S. I, Lebedev A. V.** (1981). Emulsion Polymerization and Its Applications in Industry. New York: Plenum Publishing Corporation.

[30] **Piirma I.** (1982). Emulsion Polymerization. New York:Academic Press.

[31] **Fitch M. R.** (1997). Polymer Colloids: A Comprehensive Introduction. USA: Academic Press.

[32] **Lovell P. A, El-Aasser M. S.** (1997). Emulsion Polymerization and Emulsion Polymers. England: Wiley.

[33] **Urban D, Takamura K.** (2002). Polymer Dispersions and Their Industrial Applications. *Germany: Wiley-VCH Verlag GmbH & Co.*

[34] **Hoffman F., Delbrück K.** (1909). *German Patent,* No: 250690.

[35] **Hoffman F. and Delbrück K.** (1912). *German Patent,* No: 255129.

[36] **Dinsmore R. P**. (1929). *United State Patent,* No: 1732975.

[37] **Yamak H. B.** (2013). Emulsion polymerization: Effects of polymerization variables on the properties of vinyl acetate based emulsion polymers, *Polymer Science,* 35-72.

[38] **Erbil H. Y.** (2000). Vinyl acetate emulsion polymerization and copolymerization with acrylic monomers, *Florida: CRC Pres.*

[39] **Chern C. S.** (2006). Emulsion polymerization mechanisms and kinetics. *Polym. Sci.***,** ***31****,* 443-486.

[40] **Lijen C, Shi Y. L, Chorng S.C, Shuo C.W**. (1997). Critical Micelle Concentration of Mixed Surfactant SDS/NP$(EO)_{40}$ and Its Role in Emulsion Polymerization. *Colloids and Surfaces,* ***122****,* 161-168.

[41] **Chern C.S, Lin S.Y, Chang S.C, Lin J.Y, Lin Y.F.** (1998). Effect of initiator on styrene emulsion polymerisation stabilised by mixed SDS/NP-40 surfactants. *Polymer*, ***39****,* 2281-2289.

[42] **Javier I, Amalvy M. J, Unzué H. A. S, José M. A.** (2002). Reactive surfactants in heterophase polymerization: Colloidal properties, film-water absorption and surfactant exudation, *J. Polym. Sci.,* ***40****,* 2994–3000.

[43] **Guyot A, Tauer K, Asua J. M, Van S, Gauthier C, Hellgren A. C, Sherrington D. C, Goni A. M, Sjoberg M, Sindt O, Vidal F, Unzue M, Schoonbroad H, Shipper E, Desmazes P.L. (**1999). Reactive surfactants in heterophase polymerization. *Acta Polym,* ***50****,* 57-66.

[44] **Harkins W. D.** (1945). A general theory of the reaction loci in emulsion polymerization, *J. Chem. Phys*., ***13***, 381.

[45] **Harkins W. D**. (1946). A general theory of reaction loci in emulsion polymerization. *J. Chem. Phys.*, ***14***, 47-48.

[46] **Gardon J. L**. (1968). Emulsion polymerization I. Recalculation and Extension of Smith- Ewart Theory, *J. Polym. Sci,* ***6***, 623-641.

[47] **Blackley D. C.** (1997). Polymer latices science and technology, ***2***, *London: Chapman & Hall.*

[48] **Sajjadi S, Brooks B. W. (**2000). Semibatch emulsion polymerization reactors: Polybutyl acrylate case study, *Chem. Eng. Sci.* ***55***, 4757-4781.

[49] **Sajjadi S**. (2000). Particle formation and coagulation in the seeded semibatch emulsion polymerization of butyl acrylate, *J. Polym. Sci.*, ***38***, 3612-3630.

[50] **Sajjadi S**. (2001). Particle formation under monomer-starved conditions in the semibatch emulsion polymerization of styrene, *J. Polym. Sci.*, ***39***, 3940-3952.

[51] **Mayer M. J. J, Meuldijk J, Thoenes D.** (1994). Emulsion polymerization in various reactor types: Recipes with high monomer content, *Chem. Eng. Sci.*, ***49***, 4971-4980.

[52] **Gupta V. K, Bhargava G. S, Bhattacharyya K. K.** (1980). *J. Macromol. Sci Pure Appl. Chem.*, A16, ***6***, 1107.

[53] **Rahmani S, Entezami A. A**. 2011, *Macromol. Res.*, ***19 (3)***, 221.

[54] **Oliveira P.C, Guimarães A, Cavaillé J-Y, Chazeau L, Gilbert R. G, Santos A. M**. (2005). *Polymer*, ***46***, 110.

[55] **Pham T.T. B, Fellows C. M, Gilbert R. G**. (2004). *J. Polym. Sci. A. Polym. Chem.*, ***42,*** 3404.

[56] **Chung T. C**. (2002). Prog. Polym. Sci., ***27,*** 39.

[57] **Galia A, De Gregorio R, Spadaro G, Scialdone O, Filardo G. (**2004). *Macromolecules*, ***37***, 4580.

[58] **Tsuchida A, Suda M, Otha M, Yamauchi T, Tsubokawa N**. (2006). *J. Polym. Sc.i A. Polym. Chem.*, ***44***, 2972.

[59] **Yang W, Rånby B.** (1996). *J. Appl. Polym. Sci.*, ***62,*** 533.

[60] **Sakurai K, Kondo Y, Miyazaki K, Okamoto T, Irie S, Sasaki T**. (2004). *J. Polym. Sci. B. Polym. Phys.*, ***42,*** 2595.

[61] **Teare D. O. H, Schofield W. C. E, Garrod R. P, Badyal J. P. S**. (2005). *Langmuir*, ***21(23),*** 10818.

[62] **Shao H. J, Guo J. B, Li Y. J, Yu J, Qin S. (**2011). *Adv Mater. Res.*, ***1153,*** 239−242.

[63] **Rempp P. F, Lutz P. J.** (1989). In Comprehensive Polymer Science, *Pergamon Press, Oxford.*

[64] **Pitsikalis M, Pispas S, Mays J. W, Hadjichristidis N.** (1998). Comparison and classification of controlled/living radical polymerizations, *Adv. Polym. Sci.*, ***135***, 1.

[65] **Schutz G. O, Milkovich R. J.** (1982). Graft polymers with macromonomers: synthesis from methacrylate-terminated polystyrene, *J. Appl. Polym. Sci.*, ***27***, 4773-4786.

[66] **Mishra M. K**. (1994). Macromolecular design: concept and practice, *Polymer Frontier International, New York.*

[67] **Radke W, Müller A. H**. (1993). Copolymerization of PMMA macromonomers with methacrylate and N-butyl acrylate and characterization on resulting graft copolymers, *Division of Polymer Chemistry, **34**,* 652.

[68] **Shinoda H, Matyjaszewski K.** (2001). Structural control of poly (methyl methacrylate)-g-poly (lactic acid) graft copolymers by atom transfer radical polymerization (ATRP), *Macromolecules, **34,*** 6243-6248.

[69] **Shinoda H, Miller P. J, Matyjaszewski K.** (2001). Improving the structural control of graft copolymers by combining ATRP with the macromonomer method, *Macromolecules, **34,*** 3186-3194.

[70] **Sheiko S. S, Sumerlin B. S, Matyjaszewski K.** (2008). *Prog Polym Sci., **33,*** 759.

[71] **Abbrasian M. J.** (2011). *Elastom Plast., **43 (5)**,* 481.

[72] **Bonilla-Cruz J, Guerrero-Sánchez C, Schubert U. S, Saldívar-Guerra E**. 2010, *Eur. Polym. J.,* **46**, 298.

[73] **Bonilla-Cruz J, Saldívar-Guerra E, Torres-Lubián J. R, Guerrero-Santos R, López-Carpy B, Luna-Bárcenas G.** (2008). *Macromol. Chem. Phys., **209,*** 2268.

[74] **Von Werne T, Patent T: E.** (1999). Preparation of structucally well-defined polymer-nanoparticle hybrids with controlled/living radical polymerizaitons, *J. AM. Chem. Soc., **121**,* 7409-7410.

[75] **Pyun J, Matyjaszewski K, Kowalewski T, Savin D, Patterson G, Kickelbick G, Huesing N.** (2001). Synthesis of well-defined block copolymers tethered to polysilsesquioxane nanoparticles and their nanoscale morphology on surfaces, *J. Am.Chem. Soc., **123**,* 9445-9446

[76] **Matyjaszewski K, Miller P. J, Shukla N, Immaraporn B, Gelman A, Luokala B. B, Siclovan T. M, Kickelbick G, Vallant T, Hoffman H, Pakula T. (**1999). Polymers at interfaces: using atom transfer radical polymerization in the controlled growth of homopolymers and block copolymers from silicon surfaces in the absence of untethered sacrificial initiator, *Macromolecules, **32**,* 8716-8724.

[77] **Husseman M, Russell T. P, Hawker C. J, Huang E.** (1999). Polymers at interfaces: using atom transfer radical polymerization in the controlled growth of homopolymers and block copolymers from silicon surfaces in the absence of untethered sacrificial initiator, *American Chem. Soc., **40**,* 112-113.

[78] **Subramaniam A**. (1999). Natural rubber, *Morton M. (ed), Rubber Technology*, 179-208.

[79] **Mathew N. M.** (2001). Natural rubber, *White J. R (ed.) Rubber Technologist's Handbook*, 11-45.

[80] **Campbell D. S.** (1992). Natural rubber: biology, cultivation and technology, *Elsevier Science Publishers,* 451.

[81] **Subramaniam A.** (1972). *Rubber Chemistry and Technology, **45(1),*** 346.

[82]**Subramaniam A**. (1975). *Proceedings of the International Rubber Conference, Kuala Lumpur IV, **3***.

[83] **Montes S, White J. L.** (1982). *Rubber Chemistry and Technology, **55(5)***, 1354.

[85] **Bristow M.** (1979). *NR Technology*, ***10(3),*** 53.

**CURRICULUM VITAE**

## Personal Information

| | | |
|---|---|---|
| Date of Birth | : | 08.09.1986 |
| Place of Birth | : | Istanbul |
| Driving License | : | Class B (Since 2010) |

## Education

| | |
|---|---|
| 2012-to date | Istanbul Technical University, Faculty of Science and Letters, Polymer Science and Technology<br>Master of Science |
| 2004-2010 | Middle East Technical University, Faculty of Science and Letters, Chemistry |
| 2000-2004 | Vefa Anatolian High School, Istanbul |

## Employment

| | |
|---|---|
| Jan, 2015- to date | R&D Engineer, Modern Ambalaj |
| Mar, 2014–Jan, 2015 | R & D Engineer, CHT Textile Chemicals |
| Dec, 2013-Feb, 2014 | Product Manager, Ravago Group /Resinex-BMY |
| June, 2013-Dec, 2013 | Sales Executive, Ravago Group /Resinex-BMY |
| May, 2010-Apr, 2013 | Sales & Application Specialist, Terralab Lab. Equip. |

## Trainings & Congress

Pigment Dispersion and Stabilization, 2014
Formulations of Pressure Sensitive Adhesives, 2014
Ampacet Technical Training @ Luxemburg, 2014
Styron Products Training @Netherlands, 2013
Methods of Injection Technologies, 2013
National Nanoscience and Nanotechnology Conference, 2012
International Pharmaceutical Science Symposium, 2012
ISO 9001:2008 Quality Management System Training, 2011